



Micromethods of
QUANTITATIVE ORGANIC
ANALYSIS

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PREFACE TO THE SECOND EDITION

The reviews given the First Edition of this laboratory manual have encouraged the authors not only to retain and continue the mode of presentation as inaugurated therein but also to enlarge and widen the scope of the material presented. Thus, new developments in the authors' laboratory, which include the use of ordinary analytical balances in quantitative organic microanalysis, new molecular-weight determinations, and numerous other improvements and simplifications, as well as the latest and more important contributions by others, have been included in the present edition.

In this laboratory manual, the methods presented have been strictly separated from historical and discursive matters through the introduction of separate headings "remarks" and "literature" at the end of every chapter. This separation, which frees the actual working procedures from distractive matters, has the further advantage of presenting the entire development and literature of a given method in cumulative and easily surveyable form.

In the present edition, which is being published at the *thirtieth anniversary* of the introduction of practical quantitative micromethods into organic chemistry by the late Nobel laureate F. Pregl, teacher of the senior author, the literature cited comprises well above a thousand references by more than eight hundred authors, a fact which most expressively illustrates the interest and rapid progress made in this branch of science.

The authors wish to express their sincere thanks and appreciation to their colleagues, coworkers, students, and visiting professors for the many constructive suggestions which have been incorporated in this book.

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INTRODUCTION

One of the noteworthy advances in chemistry has been the introduction of methods and technics permitting chemical operations with smaller amounts of substances than commonly used, a fact well recognized in chemical research, both organic and inorganic. In certain branches of chemistry the application of micromethods has become a necessity, particularly in the field of hormones and vitamins. Numerous successful applications of microtechnic to qualitative organic chemical problems of toxicological, clinical, and pathological nature were reported in the chemical literature as early as the second part of the last century. One of the earliest contributions to this branch of science was made in the United States in 1867, in which year the monograph *Microchemistry of Poisons* by T. G. Wormley³⁹ was published.

Among the first successful attempts in quantitative organic analysis to decrease the amount of the sample from decigrams to centigrams was the molecular-weight method of G. Barger,*² published in 1904. Quantitative inorganic microanalyses appear to have been first performed in 1903 by W. Nernst and E. H. Riesenfeld,^{14, 15} when atomic-weight determinations on inorganic samples weighing 1 mg. and less were described. An empirically calibrated microbalance was used. Subsequently, in 1909, F. Emich† and co-workers reported the first quantitative milligram (micro) processes with pure organic compounds,⁹ such as a micro-Carius procedure for sulfur‡ and halogen,§ and in 1911²⁵ a micro-Kjeldahl method,|| using the microbalance of W. Nernst.^{14, 15} The substitution of this microbalance by the Kuhlmann microchemical balance in quantitative microanalysis was recommended by J. Donau⁵ in 1911.

Using this balance, F. Pregl¶ succeeded in the same year²⁸ in revolutionizing most of the existing macrochemical methods in quantitative organic analysis of pure organic compounds by the introduction of

* 31-mg. sample.

† Died January 22, 1940.

‡ 0.3- to 1-mg. samples.

§ 1- to 3-mg. samples.

|| 0.4- to 2-mg. samples.

¶ Died December 13, 1930.

equivalent micromethods. These procedures permitted determinations with samples amounting to a few milligrams and involved not only manipulative microtechnic, but also complete co-ordination of apparatus designs to such processes.²⁸⁻³³ In the subsequent and widespread use of the Pregl microanalytical methods for pure organic substances, the saving in material and time—features which are usually associated with and demanded of microchemical procedures—were decisive contributing factors. Their practicability was an additional advantage which gradually led to a complete replacement of the corresponding macromethods used heretofore.¹⁶ This general adaptation of the milligram processes brought about the introduction of these methods both in industrial organic research laboratories and in the teaching curricula of institutions offering advanced chemical instruction.

Certain difficulties arose in the transfer in 1925 of the microprocedures from the ideal location and laboratory arrangements as provided in F. Pregl's own institute at the University of Graz, Austria, to the authors' laboratory at New York University, Washington Square College, New York, N. Y., U. S. A. With the subsequent systematic teaching of these methods by the authors^{16a} within the set framework of a graduate laboratory course (Chemistry 202) further difficulties had to be overcome, which necessitated the changes in the above microprocedures as presented in the first¹⁹ and continued in the present edition of this book.*

In the present edition the chapters on balances and weighing have been enlarged to include the use of ordinary analytical balances of proper sensitivity and precision.¹⁷ Additional paragraphs treating the calibration of weights, the determination of the zero reading, and the determination of the sensitivity and precision of the microanalytical as well as the ordinary analytical balance have also been included in the present volume.

To the changes in the carbon and hydrogen determination^{3, 13, 16c, 18, 19, 28-33, 38} as given in the first edition, which included a practical preheater, the side-arm combustion tube, combustion in oxygen, new absorption reagents, as well as an aspirator for the absorption tubes, have been added several types of combustion-tube fillings.^{19a} Wet combustion methods for the determination of carbon are also discussed, and the manometric method of D. D. Van Slyke and J. Folch³⁷ has been described in detail in the present edition.

* Reviews of the first edition: *J. Am. Chem. Soc.*, **61**, 2985 (1939); *Ind. Eng. Chem., News Ed.*, **16**, 241 (1938); *Analyst*, **63**, 467 (1938); *Microchemie*, **24**, 237 (1938); *Z. anal. Chem.*, **113**, 293 (1938); *J. Indian Chem. Soc.*, **15**, 404 (1938); *J. Chem. Soc., Japan*, **59**, 966 (1938); etc.

The volumetric determination of aminoid nitrogen (Kjeldahl method) remained unchanged from the original Pregl procedure³⁰⁻³⁴ also in the present edition. The improvements in the gasometric determination of nitrogen (Dumas method), which included a double Kipp generator and the introduction of a gasometer,^{20, 21, 36} by means of which the amount of carbon dioxide used in the combustion and sweeping-out process is measured, have been retained unchanged from the first edition.

The determinations of halogen and sulfur have been improved,²⁷ while the wet combustion method of M. K. Zacherl and H. G. Krainick⁴⁰ and the bomb method of A. Elek and D. W. Hill,⁸ which were introduced in the first edition, have been retained in the present volume. The same is true of the application of F. Emich's immersion filter,¹⁰ as recommended by W. Saschek³⁴ for the filtration of barium sulfate. The use of a platinum cylinder in the determination of metals, as suggested by H. K. Alber¹ and H. I. Coombs,⁴ is also retained.

The standard solutions have now been unified in a single chapter, and with the introduction of the 0.01 *N* potassium biiodate solution, which takes the place of the 0.01 *N* hydrochloric acid solution, the preparation and standardization of the 0.01 *N* solutions used in titrimetric procedures have been simplified. To the ebullioscopic, cryoscopic, and vaporimetric molecular-weight methods has been added an isothermic method.^{16b, 22-25} Liberal time estimates have been given for all the more important determinations in order to facilitate the planning of a day's working or teaching schedule.

The structure analytical methods include the determination of active hydrogen by A. Soltys,³⁵ the acyl determination of R. Kuhn and H. Roth,¹² the alkoxyl and acetyl groups determinations of A. Elek⁶ and A. Elek and R. A. Harte,⁷ respectively, and the modified alkimide group determination of A. Friedrich.¹¹

The literature has been brought up to 1941. In the Appendix are chapters pertaining to qualitative organic analysis,^{16d} to the teaching of quantitative organic elementary micromethods,^{16a} and to the installation of a laboratory for quantitative organic microanalysis in colleges, research institutions, and organic research laboratories in industry.

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THE BALANCE

In principle any balance showing a reproducible sensitivity, or precision, of 0.001 to 0.020 milligram can be used for quantitative organic microanalysis. Two types of balances are employed: a microanalytical balance, or an ordinary analytical balance.

Required Precision

A direct relationship exists between the precision of a balance intended for use in quantitative organic microanalytical procedures³³ and the amount of substance to be used. This relationship is illustrated in the table below.

| PRECISION OF BALANCE | AMOUNT OF SAMPLE | |
|-------------------------|--|---|
| | <i>Theoretical Minimum⁹</i> | <i>Practical Average³³</i> |
| mg. | mg. | mg. |
| 0.001 | 0.3-0.4 | 3- 5 |
| 0.002 | 0.6-0.8 | 4- 6 |
| 0.005 | 1.5-2.0 | 5- 8 |
| 0.010 | 3.0-4.0 | 6-10 |
| 0.020 | 6.0-8.0 | 8-12 |

For all practical purposes a microanalytical balance should have a minimum precision of ± 5 micrograms,* for a load up to 1 gram and of ± 10 micrograms for loads above 1 gram. Numerous domestic^{2, 7, 35} as well as foreign-made^{11, 24, 26, 27, 30, 34, 39, 42} microanalytical balances fulfill these requirements.^{1, 12, 13, 19, 21, 23, 29, 38, 41} In keeping with the above it should be borne in mind that the claim often made, but rarely fulfilled, that a microanalytical balance has a precision of ± 1 microgram at a maximum load of 20 grams should not be interpreted as an essential requirement for quantitative organic microanalysis.

An ordinary analytical balance intended for use in quantitative organic microanalysis should show a minimum precision of at least 1/50 milligram for loads not exceeding 10 grams.^{33, 37a, 49} In actual practice balances which show a precision of 1/100 milligram will be found

* One microgram = 0.001 milligram = 1 gamma (γ).

most useful. Several makes of domestic balances^{2, 7, 43} are available, which sometimes are called *semi-micro* or *precision-analytical* balances, that show this precision and also conform to the standard methods of testing of workmanship and satisfactory performance of analytical balances.^{1, 14, 22, 28, 40}

THE MICROANALYTICAL BALANCE

Description

As a typical microanalytical balance, the microchemical balance of Wm. F. Kuhlmann,²⁴ which was extensively employed by F. Pregl,³⁷ is herewith described in detail. The balance consists of the balance case, the black glass base, and the weighing mechanism. The last operates through the hollow center column which is mounted on the base and supports the fulcrum. On the fulcrum rests the balance beam, which is a platinum-plated flat sheet of metal shaped somewhat like the letter K. The upper horizontal part of the beam is 7 cm. long and carries the rider scale, which has 101 notches with corresponding numerical marks from 0 to 10 below each tenth notch. The rider scale is so calibrated that the first notch at the end of the beam represents zero, each successive notch 0.1 milligram, and the numerical marks whole milligrams when a 5-mg. rider is used. The center of the beam carries an agate knife edge which faces the agate plate of the fulcrum, and each terminal of the beam is provided with an upright knife edge which contacts the agate plate of the corresponding stirrup. These three agate knife edges must be parallel to each other and in one plane, as well as equidistant from the center. The arrestment rod extends through the hollow center column and carries a horizontal bar provided with three arrestment cups in the front and three arrestment slots in the rear, of which one cup and slot are located in the center and one of each at the left and right terminal.

The horizontal metal part of each stirrup is provided with an agate plate in the center and an agate contact point in the front as well as in the rear which fits into the corresponding agate cup or slot. To prevent the interchange of the stirrups in assembling the balance they are marked with dots which must face forward and coincide with the corresponding marks on the arrestment bar. S-shaped wire hooks, inserted at the acute angle or lowest part of the stirrups, serve for the attachment of the weighing pans. Suitably bent hooks for the support of tubes used in weighing are attached to the suspension wires of the left weighing pan or of both weighing pans.

The pointer, which is 13.5 cm. long, is attached to the center of the beam and extends down to the pointer scale at the base of the center column. The pointer scale is 22 mm. in length and has 12 divisions on each side of the zero line.

The rider used in the balance is made of aluminum, weighs 5 mg., and is shaped like an inverted V, with loops at the apex and terminals. Suitable magnifying devices at the rider and the pointer scale facilitate reading the respective scale. The magnifying device for the pointer

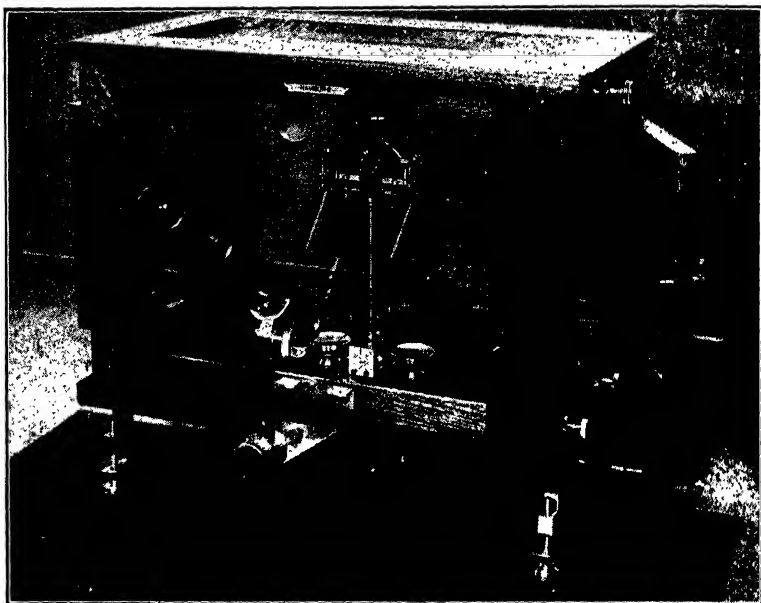


Fig. 1. Typical Microanalytical Balance.

scale should be so arranged as to avoid, or at least keep at a minimum, any parallax errors.

In the Kuhlmann telescope balance²⁴ shown in Fig. 1 a telescope is attached to the base of the front window. The pointer carries a small disk of approximately 3-mm. diameter. This disk, which is in the focus of the telescope, takes the place of the usual pointer scale and swings with the pointer; a stationary hair line in the eyepiece of the telescope serves as the reference line. Owing to the shortness of the swings in this balance, greater constancy and, consequently better reproducibility of weighings are obtainable.

Installation

Since a temperature change of 1 to 2° C. will cause a shift of approximately 10 micrograms^{36, 41} in the zero reading, a temperature constancy of $\pm 2^\circ$ C. is highly desirable. A room should be chosen in which a fairly constant temperature can be maintained while the balance is in use. For the same reason the balance should be placed well away from radiators or heat-radiating devices and should not be exposed to direct sunlight. Artificial light sources should be at least 3 ft. away. Under adverse conditions it would be well to construct a special balance compartment which would allow free circulation of air and yet prevent exposure of the balance to heat or drafts. Satisfactory set-ups for micro-analytical balances have been described repeatedly.^{3, 4, 6, 10, 12, 13, 21, 23}

Although humidity as a rule does not interfere to any extent with the satisfactory performance of the balance, nevertheless it may cause the beam to stick and prevent the free swinging of the pointer upon release of the arrestment. The ideal humidity is considered to be about 50%. A lower moisture content of the air may permit the accumulation and retention of electrostatic charges on the metal parts of the balance.^{37, 46} It is claimed that this condition may be remedied by grounding the balance or by placing a radioactive element in the balance case.³⁷ The balance requires also a reasonable amount of protection from vibration; usually it is sufficient to provide a solid foundation. A solid wooden table or bench with a top of marble, soapstone, or Transite provides as a rule an adequate support for the balance, although a combination of rubber sheets and lead or stone slabs, may be necessary under adverse conditions. An arrangement for a shock-proof and vibration-free support has been described by W. R. Kirner.²¹

Cleaning and Assembling

The balance, when received from the manufacturer, usually is accompanied by detailed instructions for unpacking and assembling. It is obvious that these instructions must be followed in every detail and that the proper care be exercised in unpacking and assembling the balance, especially in removing or handling the beam, in order to avoid bending the tip of the pointer. The various parts of the new balance are cleaned and assembled just as they are cleaned and assembled periodically after the balance has been in use for some time; therefore, the instructions given below for the care and cleaning of the balance apply also to a new one.

IMPLEMENTS

A sheet of glazed white paper, several thoroughly washed and dried pieces of soft thin chamois, four finger cots of rubber or chamois for thumbs and index fingers, a few round toothpicks, ivory-tipped forceps, a camel's-hair brush washed in acetone, a container with absorbent cotton, a magnifying lens, and a small flashlight are all the necessary tools needed for the cleaning of the balance.

PROCEDURE

First, the table upon which the balance is to be placed is cleaned; then the removable case, if the balance is provided with one, is taken off. In balances having a fixed case, the front window is removed and placed on top of the balance. With the index fingers and thumbs covered with the finger cots, because the metal parts of the balance should never be touched with unprotected fingers, the balance pans are taken off and placed on the glazed white paper which is spread near the balance case; the stirrups are removed next by grasping them by the horizontal metal bar and lifting them off the beam. Then the beam of the balance, being held at the upper half of the pointer, is lifted off the fulcrum and also placed on the paper with the pointer tip upward.

The inside of the balance case is cleaned by wiping it with a chamois and dusting it afterwards with a large camel's-hair brush. The axis and the three cams under the base plate are oiled with a trace of watch-maker's oil. The central agate plate on the fulcrum as well as the agate cups and slots are cleaned with a perfectly dry cotton tuft wound around a toothpick and then thoroughly brushed with a small camel's-hair brush; particular attention must be paid to this operation, because deposits of dust or fibers on the agate plate or in the cups or slots are frequently responsible for a condition known as *sticking* of the balance beam when the arrestment is released. If this sticking cannot be eliminated by ordinary cleaning or wiping of the surfaces of contact, the wiping should be repeated with a cotton tuft moistened with a trace of alcohol or acetone, followed immediately with a thorough wiping with a dry cotton tuft. Finally, the cleaned parts are brushed again and minutely examined with the aid of a small flashlight and a magnifying lens for fibers and dust particles.

The beam is cleaned next. It is held at the pointer somewhat below the horizontal bar, and the three knife edges are wiped also with a clean cotton tuft. The two contact points are treated similarly, and finally the entire beam is brushed free from dust or lint and thoroughly inspected with the aid of a magnifying lens for deposits of dust particles.

Then, with the balance arrested and the hand steadied, the beam is put on the fulcrum by placing the two contact points in the arrestment cup and slot in the front and rear of the arrestment bar.

The agate plate and the two contact points of both stirrups are cleaned with a cotton tuft and brushed, as described above. Then the stirrups are placed in the agate cups of the respective terminals of the arrestment bar so that the markings face the front and coincide with the markings on the arrestment bar. The balance pans and suspension wires are cleaned by wiping them with a chamois and brushing them afterwards. The pan marked with the letter "R" is placed on the S-shaped hook of the right-hand stirrup, and the other pan, marked with the letter "L," is placed on the left-hand stirrup. Then the rider is brushed and placed on the zero notch of the rider scale. Finally, the balance is leveled by turning the adjustment screws at the front support; the plummet in the rear of the center column, or two spirit levels, one of which is placed in front and the other parallel to one of the side doors, are used as level indicators. Then the balance case or the front window is replaced, and about 30 minutes later, during which time the side doors of the balance are left half open, the zero reading is adjusted by turning the adjustment screw on the horizontal rod back of the beam with the aid of the ivory-tipped forceps. The adjustment screw is turned forward if the pointer swings too far to the right and backward if it swings too far to the left of the zero line. However, the balance need not be adjusted to exactly zero; an adjustment which gives a zero reading between zero and ± 50 micrograms is quite satisfactory.

THE ORDINARY ANALYTICAL BALANCE

Description

Since the only difference between an analytical balance for macro-analytical and one for microanalytical work is merely an increased precision and sensitivity, there need not be any change in its construction.^{7, 33, 37a, 49} For practical purposes and for the sake of uniformity in the weighing procedure, an analytical balance intended for use in microanalytical procedures should possess the following features: The beam should be calibrated and marked from 0 to 10 milligrams,² with the zero mark under the first notch at the extreme left. Only notches denoting whole milligrams are needed, and hence the usual subdivisions representing tenths of a milligram may be omitted.⁷ A 5-milligram rider is used. The pointer scale should have at least ten divisions on

either side of the zero line and should be provided with a magnifying lens.

For continuous proper function of an analytical balance possessing a higher than ordinary precision, it is necessary, in the installation and during the process of cleaning and assembling, to observe the same precautions as for a microanalytical balance.

Remarks

The directions in regard to the performance, assembling, and cleaning of the microanalytical balance have been kept strictly within the scope of a laboratory manual and, therefore, represent the *minimum* requirements such as can be found in the average chemical laboratory. For detailed discussions concerning further refinements, the investigations of F. Emich,¹⁶ E. Schwarz-Bergkamp,⁴¹ L. Ramberg,³⁸ G. Gorbach,¹⁹ H. Sternberg,⁴⁵ A. W. Ainsworth,^{1, 29} A. H. Corwin,¹³ J. Kuck and E. Loewenstein,²³ and others^{3, 4, 6, 8, 10, 12, 17, 18, 21, 46} should be consulted.

Aside from the Kuhlmann type of microanalytical balances,²⁴ for which the term *microchemical balance* has been in vogue, a number of differently constructed microanalytical balances serving a like purpose have been described and are in actual use.^{15, 20, 23, 38, 48} One such balance²³ possesses a new rider device according to the principle of L. Ramberg.³⁸ It has a short beam with only forty notches on the rider scale. A 2-milligram quartz rod is used as rider.^{35, 39}

F. Emich,¹⁶ in his first quantitative inorganic microprocedures, used the microbalance of W. Nernst^{31, 32} which had to be calibrated empirically. Quartz spring balances of the Salvioni type can be utilized for milligram procedures and have been found particularly useful for demonstrations in lectures. A practical quartz fiber microbalance has been described by J. Donau.¹⁵ Precision balances of various designs have been used since 1886⁴⁷ for quantitative analytical procedures involving milligrams and smaller amounts of material.^{5, 20, 25, 44} For quantitative microgram procedures, such as residue determinations and electrolysis, F. Emich and E. Wiesenberger⁴⁸ employed a modified Nernst microbalance.

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WEIGHING

MICROANALYTICAL BALANCE

The microanalytical balance is considered to be in equilibrium when the 5-mg. rider rests in the first notch, which is marked zero, at the left end of the beam. Moving the rider for one notch to the right (0.1 mg.) causes a deflection of ten *divisions* of the pointer on the pointer scale, provided that the sensitivity of the balance is exactly 100. One *division* on the pointer scale thus represents 0.01 mg. Each *division* on the pointer scale is counted as 10 *deflection units*. A single *deflection unit* or "pointer-scale unit," ^{1a} is thus regarded to equal 0.001 mg., or 1 microgram, or 1 gamma (γ).

The pointer scale is calibrated to be read in the following manner: The center line where the pointer stops when the balance is arrested is considered zero; each division to the right of this zero line is counted as +10 and to the left as -10 deflection units. In practice, as a matter of simplicity, it is expedient to interpret the readings on the pointer scale as whole numbers and not as fractions, as for example, a swing of the pointer for $5\frac{1}{2}$ divisions is read as 55 deflection units, that is 55 micrograms.

The arresting mechanism of the balance functions in such a way that, when the handle attached to the arrestment mechanism outside of the balance case is partly turned, only the pans are released. If they start swinging, indicating that they are off center, they are arrested again, and this operation of arresting and releasing is repeated until the pans remain stationary. Then the balance is released completely by turning the handle backward until it comes to a stop. By releasing the arrestment properly, the amplitude of the swings of the pointer, which normally should be between 3 and 8 divisions, can be controlled; at no time should the pointer be permitted to swing beyond the scale. If the amplitude of the swings exceeds 5 divisions on any one side of the zero line, thereby giving a deflection sum in excess of 50, then the rider should be placed on the adjacent notch to obtain a deflection sum of less than 50. Upon release of the arrestment of the balance the first two swings of the pointer are ignored when the pointer started to swing from the left, and three, when from the right. The next swing, beginning

from the left, is counted, and the point of reversal of the pointer noted as illustrated below:

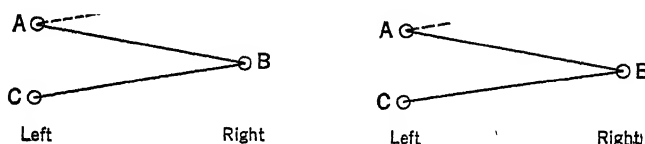


Fig. 2.

Position A: point of reversal at the left.
 Position B: point of reversal at the right.
 Position C: point of reversal at the left.

The *deflection sum* * is the algebraic sum of position B and the average of positions A and C.

After the readings have been taken the beam is arrested gradually when the pointer swings toward the zero line of the pointer scale. The deflection sum is *added* to the beam reading if *positive*, and *deducted* from the beam reading if *negative*, as illustrated by the following four examples:

| CASE | POINT OF REVERSAL | | POSITION A | POSITION C | AVERAGE OF AC | POSITION B | DEFLECTION SUM | |
|------|-----------------------------------|--------------|---------------|---------------|------------------|---------------|-------------------|------------------|
| | to the left (of the zero line) | to the right | | | | | | |
| 1 | All | | + 3 | + 5 | + 4 | +23 | +27 | to be added |
| 2 | All | | -42 | -40 | -41 | - 7 | -48 | to be subtracted |
| 3 | A,C | B | -15 | -13 | -14 | +30 | +16 | to be added |
| 4 | A | B,C | - 1 | + 3 | + 1 | +30 | +31 | to be added |

With the rider on the rider scale at 5.4 (beam reading: 5.4 mg.) the final results of the above four weighings would be as follows: case 1: 5.427 mg.; case 2: 5.352 mg.; case 3: 5.416 mg.; case 4: 5.431 mg.

Determination of the Zero Reading

The *zero reading* is defined as the *deflection sum* obtained when the balance is released with the rider at zero and the balance pans empty. The zero reading differs from the so-called zero point, which is actually one-half of the zero reading.

* The expression *deflection sum* used in this book is synonymous with the expressions *deflection*, *deflection difference*, *mean deflection*, or *Ausschlag*, used by other authors.

After the side doors of the balance have been closed the rider is placed on the first notch (0). The rider should sit straight and rest on the lowest point of the notch; to insure this the rider may have to be lifted up again and be permitted to fall into the notch, or it may be touched lightly at its apex with the hook of the rider carrier. The arresting mechanism is then released and the swings of the pointer on the pointer scale observed. This procedure is repeated until no greater deviations than ± 2 deflection units are obtained in three successive trials. This repetition of the weighings, or *checking*, is a general rule which should always be observed. If more than 30 minutes pass between two weighings of the same object, it is necessary to redetermine the zero reading and to correct for any possible deviation as explained below:

| ZERO READING | | | |
|--------------|--------|--------|------------------|
| First | Second | CHANGE | |
| -30 | -25 | 5 | to be subtracted |
| -22 | -31 | 9 | to be added |
| +17 | +28 | 11 | to be subtracted |
| +35 | +27 | 8 | to be added |

Determination of the Sensitivity and Precision

The sensitivity * of the balance is equal to the *algebraic difference* of the two deflection sums with the rider at the zero and 0.1 mg. notch, respectively.

EXAMPLE:

| | |
|--|---------------|
| Deflection sum (at notch 0)..... | +12 |
| Deflection sum (at notch 0.1 mg.)..... | <u>-(-84)</u> |
| Sensitivity of the balance..... | 96 |

If the zero reading is negative, a small object such as a lead shot is placed on the left balance pan and weighed with the rider at two adjacent notches so that both plus and minus readings are obtained. As shown in the following example:

| FIRST DETERMINATION | | SECOND DETERMINATION | |
|---------------------|-------------------|----------------------|-------------------|
| Beam reading..... | 5.300 mg. | Beam reading..... | 5.400 mg. |
| Deflection sum.... | <u>+0.021 mg.</u> | Deflection sum.... | <u>-0.075 mg.</u> |
| Weight..... | 5.321 mg. | Weight..... | 5.325 mg. |

The sensitivity of the balance in the above case is also 96 $[21 - (-75)]$. The sensitivity with a load of 10 grams is determined in a similar manner.

* The term *sensitivity* is to be interpreted as being synonymous with *sensibility*, a term also used in connection with analytical balances.⁸

The precision of the microanalytical balance ^{1, 2, 9, 24} is determined by taking a series of at least twelve readings, but always alternating the rider position between 0.0 mg. and 0.1 mg., so that six readings of each rider position are obtained.

The following tables illustrate a typical application of the foregoing procedure of determining the sensitivity and precision of a micro-analytical balance.

DETERMINATION OF THE SENSITIVITY AND PRECISION

No Load

| <i>Rider at 0.0</i> | <i>Deflection Sum</i> | <i>Rider at 0.1</i> | <i>Deflection Sum</i> |
|---|-----------------------|--|-----------------------|
| 1. $\begin{array}{r} +4 \\ +5 \\ \hline +5 \end{array} + 27$ | $+ 5 + 27 = + 32$ | 2. $\begin{array}{r} -53 \\ -49 \\ \hline -51 \end{array} - 11$ | $- 51 + (-11) = - 62$ |
| 3. $\begin{array}{r} +2 \\ +4 \\ \hline +3 \end{array} + 26$ | $+ 3 + 26 = + 29$ | 4. $\begin{array}{r} -57 \\ -52 \\ \hline -55 \end{array} - 13$ | $- 55 + (-13) = - 68$ |
| 5. $\begin{array}{r} +2 \\ +4 \\ \hline +3 \end{array} + 32$ | $+ 3 + 32 = + 35$ | 6. $\begin{array}{r} -50 \\ -48 \\ \hline -49 \end{array} - 12$ | $- 49 + (-12) = - 61$ |
| 7. $\begin{array}{r} +2 \\ +6 \\ \hline +4 \end{array} + 32$ | $+ 4 + 32 = + 36$ | 8. $\begin{array}{r} -42 \\ -39 \\ \hline -41 \end{array} - 15$ | $- 41 + (-15) = - 56$ |
| 9. $\begin{array}{r} +3 \\ +5 \\ \hline +4 \end{array} + 31$ | $+ 4 + 31 = + 35$ | 10. $\begin{array}{r} -51 \\ -49 \\ \hline -50 \end{array} - 12$ | $- 50 + (-12) = - 62$ |
| 11. $\begin{array}{r} +2 \\ +6 \\ \hline +4 \end{array} + 30$ | $+ 4 + 30 = + 34$ | 12. $\begin{array}{r} -51 \\ -48 \\ \hline -50 \end{array} - 12$ | $- 50 + (-12) = - 62$ |

SENSITIVITY

Weighings

| | |
|--------------|-------------------|
| No. 1 and 2: | $32 - (-62) = 94$ |
| 3 and 4: | $29 - (-68) = 97$ |
| 5 and 6: | $35 - (-61) = 96$ |
| 7 and 8: | $36 - (-56) = 92$ |
| 9 and 10: | $35 - (-62) = 97$ |
| 11 and 12: | $34 - (-62) = 96$ |

Average: 96

Sensitivity

0.1 milligram = 96 deflection units

1 deflection unit = 1.04 microgram (1/96)

PRECISION

| <i>Weighings</i> | | <i>Deviation from Average</i> | <i>Weighings</i> | | <i>Deviation from Average</i> |
|------------------|-----|-----------------------------------|------------------|-----|-----------------------------------|
| No. 1: | +32 | 1 | No. 2: | -62 | 0 |
| 3: | +29 | 4 | 4: | -68 | 6 |
| 5: | +35 | 2 | 6: | -61 | 1 |
| 7: | +36 | 3 | 8: | -56 | 6 |
| 9: | +35 | 2 | 10: | -62 | 0 |
| 11: | +34 | 1 | 12: | -62 | 1 |
| Average: 33 | | 13 ÷ 6 = | Average: 62 | | 13 ÷ 6 = 2.2 |

*Precision:**

No better than ± 2 deflection units (± 2.08 micrograms)

* The precision (reproducibility of weighings) of a balance cannot be better than its sensitivity and should be expressed in whole deflection units, since it is not possible to read the pointer scale more accurately than ± 1 deflection unit. To judge the weighing performance of a microanalytical balance or an ordinary analytical balance used in micro work, both the sensitivity and precision must be given.

10-GRAM LOAD

| <i>Rider at 0.0</i> | <i>Deflection Sum</i> | <i>Rider at 0.1</i> | <i>Deflection Sum</i> |
|-------------------------|-----------------------|----------------------------|-----------------------|
| 1. 0 + 67 +6 +3 | + 3 + 67 = + 70 | 2. -32 + 15 -28 -30 | - 30 + 15 = - 15 |
| 3. +5 + 60 +9 +7 | + 7 + 60 = + 67 | 4. -30 + 14 -25 -27 | - 27 + 14 = - 13 |
| 5. +1 + 68 +7 +4 | + 4 + 68 = + 72 | 6. -41 + 31 -35 -38 | - 38 + 31 = - 7 |
| 7. +3 + 60 +9 +6 | + 6 + 60 = + 66 | 8. -29 + 14 -24 -26 | - 26 + 14 = - 12 |
| 9. 0 + 64 +6 +3 | + 3 + 64 = + 67 | 10. -32 + 15 -26 -29 | - 29 + 15 = - 14 |
| 11. +2 + 61 +7 +4 | + 4 + 61 = + 65 | 12. -39 + 26 -33 -36 | - 36 + 26 = - 10 |

SENSITIVITY

Weighings

| | |
|--------------|-------------------|
| No. 1 and 2: | $70 - (-15) = 85$ |
| 3 and 4: | $67 - (-13) = 80$ |
| 5 and 6: | $72 - (-7) = 79$ |
| 7 and 8: | $66 - (-12) = 78$ |
| 9 and 10: | $67 - (-14) = 81$ |
| 11 and 12: | $65 - (-10) = 75$ |

Average: 80

Sensitivity

0.1 milligram = 80 deflection units

1 deflection unit = 1.25 microgram (1/80)

PRECISION

| <i>Weighings</i> | | <i>Deviation from Average</i> | <i>Weighings</i> | | <i>Deviation from Average</i> |
|------------------|-----|-----------------------------------|------------------|-----|-----------------------------------|
| No. 1: | +70 | 2 | No. 2: | -15 | 3 |
| 3: | +67 | 1 | 4: | -13 | 1 |
| 5: | +72 | 4 | 6: | -7 | 5 |
| 7: | +66 | 2 | 8: | -12 | 0 |
| 9: | +67 | 1 | 10: | -14 | 2 |
| 11: | +65 | 3 | 12: | -10 | 2 |
| Average: | 68 | $13 \div 6 = 2.2$ | Average: | 12 | $13 \div 6 = 2.2$ |

*Precision:*Not better than ± 2 deflection units (± 2.5 micrograms)

The foregoing experiments indicate that this particular microanalytical balance has a sensitivity of 96 when without a load, meaning that 1 deflection unit corresponds to 1/960 mg., or 1.04 microgram. This would indicate good balance performance; however, the precision experiments indicate that weighing results cannot be reproduced better than within ± 2 deflection units (± 2.08 micrograms) at no load. With a 10-gram load the sensitivity dropped to 80, with 1 deflection unit corresponding to 1.25 microgram, while the precision, reproducibility of weighings, still remained at ± 2 deflection units which now represent ± 2.5 micrograms. In other words a sample can be weighed on this balance to within ± 2.08 micrograms (maximum error: 4.16 micrograms) and an object weighing not more than 10 grams to within ± 2.5 micrograms (maximum error: 5.0 micrograms).

The foregoing sensitivity and precision determinations are actual students' (beginners') experiments, performed on a microanalytical balance which has been in continuous use for sixteen years.

Sensitivity Correction Table

The sensitivity of a microanalytical balance is seldom precisely 100, but more often between 80 and 105. If the sensitivity is between 95 and 105, it is not necessary to correct for it because then the error is within the error of estimation of the deflection units. However, if the sensitivity is either below or above these figures, then the necessary corrections should be applied. For instance, if the sensitivity of the balance is 82, the correction is obtained by dividing the theoretical sensitivity (100) by the actual sensitivity (82), $100 \div 82 = 1.22$; therefore, each 0.001 mg. or, better, each deflection unit, represents an actual value of 0.00122 mg., and 0.00022 mg. is added to every 0.001 mg. irrespective whether the reading is plus or minus. In actual practice however, a correction is made only if the error due to the deviation of the actual sensitivity from the theoretical 100 exceeds the precision required for the object to be weighed, and then the necessary correction should be applied as shown in the correction table below. Such a correction table needs to be calculated only to 50, the practical deflection sum limit.

CORRECTION TABLE

| <i>Actual Reading (Deflection Units)</i> | <i>Corrected Values (Micrograms)</i> |
|--|--|
| 1 | 1 |
| 5 | 6 |
| 10 | 12 |
| 15 | 18 |
| 20 | 24 |
| 30 | 37 |
| 40 | 49 |
| 50 | 61 |

Adjustment of the Sensitivity

If the sensitivity of the microanalytical balance with no load falls below 80 it may be necessary to adjust its sensitivity to, or near to, the theoretical 100. It is a rather difficult and tedious assignment to adjust the sensitivity to exactly 100, but since a balance having a sensitivity ranging between 95 and 105 permits weighing without the necessity of making sensitivity corrections, an adjustment between the above figures is entirely satisfactory.

To adjust the sensitivity of the microanalytical balance, first the pans, then the stirrups and the beam, are removed. The beam is held at the terminals between the index finger and thumb of the left hand and, with the rider scale facing the operator, the sensitivity screw back of

the beam is turned to the left, or upward, if the sensitivity is to be raised, and to the right, or downward, if it is to be lowered. A lowering of the sensitivity is seldom necessary. No definite statement can be made just how much the screw should be turned to obtain a given sensitivity, but as a rule, a quarter turn in the proper direction will raise or lower the sensitivity by about 5. It is advisable to write down not only how much the screw has been turned, but also the direction in which it was turned, because this operation, including the testing which follows, may take several days before a proper adjustment is obtained and one may forget in the ensuing intervals just what has been done. Furthermore, the sensitivity screw should never be given more than a quarter turn at one time, because only then will the operator become aware of the respective changes of the sensitivity obtained, a fact which not only will be of value when future adjustments are attempted, but also will prevent a destructive disturbance of the sensitivity mechanism. It should also be emphasized that the sensitivity screw should be turned with the fingers and not with pliers or forceps and that all application of force must be avoided. The balance is then reassembled and the change in the sensitivity determined after an elapse of at least three hours. If necessary the above operation is repeated until the desired sensitivity has been obtained.

Should the balance show the proper sensitivity at no load but drop considerably with a 10-gram load—that is, drop more than 10 points—then an adjustment as described above will be of no avail, because under such conditions the balance, that is, the beam as well as the knife edges, may show defects which can be repaired only by balance experts or by the manufacturer of the balance.

ORDINARY ANALYTICAL BALANCE

An ordinary analytical balance suitable for quantitative micro determinations may be selected from a number of balances available, by systematically determining their sensitivity and precision in the manner outlined below and then choosing one which conforms to, or still better exceeds, the practical minimum requirements of precision stated on p. 6. Also any of the so-called *semi-micro* or *precision analytical* balances available on the market may be used, but nevertheless should be subjected to the same determination of precision and sensitivity.

Since the weighings on such an analytical balance are performed

exactly like those on the microanalytical balance, its beam should have the customary 10-mg. rider scale, the zero mark being at the left terminal, the 5-mg. mark in the center, and the 10-mg. mark at the right terminal. Only the whole milligram notches are necessary, and hence the subdivisions denoting tenths of a milligram may be omitted. Conforming to the above arrangement of the rider scale, the balance must be adjusted so that it is in equilibrium when the rider rests on the zero mark at the left end of the beam. The pointer scale of such a balance should possess accurately spaced divisions, because it is read just like the pointer scale of the microanalytical balance. The value for each *deflection unit*, one-tenth of one division on the pointer scale, in terms of micrograms has to be determined separately for every balance. Therefore, depending upon the sensitivity and precision of such a balance, a single *deflection unit*—the estimated tenth of each division—may correspond to anywhere between 5 and 20 micrograms.

Determination of the Zero Reading

As with the microanalytical balance, the zero reading of an ordinary analytical balance to be used in micro work is also defined as the *deflection sum* determined with the balance pans empty and the 5-mg. rider at the zero mark. A zero reading taken in this manner differs from the actual zero point, which corresponds to half of the zero reading. The procedure for this determination, that is the reading of the point of reversal of the pointer, is exactly the same as given for the determination of the zero reading of the microanalytical balance. The *deflection units* of every swing of the pointer on the pointer scale are noted and from the figures obtained the *deflection sum* is calculated. In this case the deflection sum denotes merely deflection units, the value of which in terms of milligrams, or micrograms, is calculated after the sensitivity and precision of the balance have been determined.

Determination of the Sensitivity and Precision

The sensitivity and precision of an analytical balance intended for use in quantitative microanalysis are determined in the same manner as described for the microanalytical balance. The rider, however, is shifted one whole milligram division, instead of 0.1 mg. as with the microanalytical balance.

The tables below furnish an actual example of the results obtained from an analytical balance used in microanalytical work.

DETERMINATION OF SENSITIVITY AND PRECISION

No Load

| <i>Rider at 0.0</i> | <i>Deflection Sum</i> | <i>Rider at 1.0</i> | <i>Deflection Sum</i> |
|--|-----------------------|---|-----------------------|
| 1. $\begin{array}{r} -32 \\ -29 \\ +46 \end{array}$ | $+46 - 31 = +15$ | 2. $\begin{array}{r} -96 \\ -93 \\ +6 \end{array}$ | $-95 + 6 = -89$ |
| -31 | | -95 | |
| 3. $\begin{array}{r} -16 \\ -14 \\ +31 \end{array}$ | $+31 - 15 = +16$ | 4. $\begin{array}{r} -114 \\ -112 \\ +26 \end{array}$ | $-113 + 26 = -87$ |
| -15 | | -113 | |
| 5. $\begin{array}{r} -28 \\ -26 \\ +42 \end{array}$ | $+42 - 27 = +15$ | 6. $\begin{array}{r} -97 \\ -94 \\ +7 \end{array}$ | $-96 + 7 = -89$ |
| -27 | | -96 | |
| 7. $\begin{array}{r} -24 \\ -23 \\ +39 \end{array}$ | $+39 - 24 = +15$ | 8. $\begin{array}{r} -103 \\ -100 \\ +12 \end{array}$ | $-102 + 12 = -90$ |
| -24 | | -102 | |
| 9. $\begin{array}{r} -19 \\ -17 \\ +33 \end{array}$ | $+33 - 18 = +15$ | 10. $\begin{array}{r} -94 \\ -92 \\ +4 \end{array}$ | $-93 + 4 = -89$ |
| -18 | | -93 | |
| 11. $\begin{array}{r} -61 \\ -57 \\ +73 \end{array}$ | $+73 - 59 = +14$ | 12. $\begin{array}{r} -94 \\ -93 \\ +5 \end{array}$ | $-94 + 5 = -89$ |
| -59 | | -94 | |

SENSITIVITY

Weighings

- No. 1 and 2: $15 - (-89) = 104$
 3 and 4: $16 - (-87) = 103$
 5 and 6: $15 - (-89) = 104$
 7 and 8: $15 - (-90) = 105$
 9 and 10: $15 - (-89) = 104$
 11 and 12: $14 - (-89) = 103$

Average: $\underline{104}$

Sensitivity

1 milligram = 104 deflection units

1 deflection unit = 9.6 micrograms (1/104)

PRECISION

| <i>Weighings</i> | <i>Deviation from Average</i> | <i>Weighings</i> | <i>Deviation from Average</i> |
|------------------|-----------------------------------|------------------|-----------------------------------|
| No. 1: +15 | 0 | No. 2: -89 | 0 |
| 3: +16 | 1 | 4: -87 | 2 |
| 5: +15 | 0 | 6: -89 | 0 |
| 7: +15 | 0 | 8: -90 | 1 |
| 9: +15 | 0 | 10: -89 | 0 |
| 11: +14 | 1 | 12: -89 | 0 |
| Average: +15 | $2 \div 6 = 0.33$ | Average -89 | $3 \div 6 = 0.5$ |

Precision:

Not better than ± 1 deflection unit (± 9.6 micrograms)

10-GRAM LOAD

| <i>Rider at 0.0</i> | <i>Deflection Sum</i> | <i>Rider at 1.0</i> | <i>Deflection Sum</i> |
|--|-----------------------|--|-------------------------|
| 1. $\begin{array}{r} -17 \\ -16 \end{array} + 19$ | $+ 19 - 16 = + 3$ | 2. $\begin{array}{r} -98 \\ -95 \end{array} - 5$ | $- 96 + (-5) = - 101$ |
| -16 | | - 96 | |
| 3. $\begin{array}{r} -18 \\ -16 \end{array} + 19$ | $+ 19 - 17 = + 2$ | 4. $\begin{array}{r} -104 \\ -100 \end{array} 0$ | $- 102 + (0) = - 102$ |
| -17 | | -102 | |
| 5. $\begin{array}{r} -15 \\ -15 \end{array} + 18$ | $+ 18 - 15 = + 3$ | 6. $\begin{array}{r} -95 \\ -93 \end{array} - 6$ | $- 94 + (-6) = - 100$ |
| -15 | | - 94 | |
| 7. $\begin{array}{r} -21 \\ -19 \end{array} + 24$ | $+ 24 - 20 = + 4$ | 8. $\begin{array}{r} -100 \\ -97 \end{array} - 2$ | $- 99 + (-2) = - 101$ |
| -20 | | - 99 | |
| 9. $\begin{array}{r} -18 \\ -16 \end{array} + 20$ | $+ 20 - 17 = + 3$ | 10. $\begin{array}{r} -97 \\ -94 \end{array} - 3$ | $- 96 + (-3) = - 99$ |
| -17 | | - 96 | |
| 11. $\begin{array}{r} -25 \\ -23 \end{array} + 26$ | $+ 26 - 24 = + 2$ | 12. $\begin{array}{r} -101 \\ -98 \end{array} - 2$ | $- 99 + (-2) = - 101$ |
| -24 | | - 99 | |

WEIGHING

SENSITIVITY

Weighings

| | |
|--------------|------------------|
| No. 1 and 2: | 3 - (-101) = 104 |
| 3 and 4: | 2 - (-102) = 104 |
| 5 and 6: | 3 - (-100) = 103 |
| 7 and 8: | 4 - (-101) = 105 |
| 9 and 10: | 3 - (- 99) = 102 |
| 11 and 12: | 2 - (-101) = 103 |

Average: 103

Sensitivity

1 milligram = 103 deflection units

1 deflection unit = 9.7 micrograms (1/103)

PRECISION

| <i>Weighings</i> | | <i>Deviation from Average</i> | <i>Weighings</i> | | <i>Deviation from Average</i> |
|------------------|----|-----------------------------------|------------------|------|-----------------------------------|
| No. 1: | +3 | 0 | No. 2: | -101 | 0 |
| 3: | +2 | 1 | 4: | -102 | 1 |
| 5: | +3 | 0 | 6: | -100 | 1 |
| 7: | +4 | 1 | 8: | -101 | 0 |
| 9: | +3 | 0 | 10: | - 99 | 2 |
| 11: | +2 | 1 | 12: | -101 | 0 |
| Average: | 3 | 3 ÷ 6 = 0.5 | Average: | 101 | 4 ÷ 6 = 0.66 |

*Precision:*Not better than ± 1 deflection unit (± 9.7 micrograms)

The foregoing weighing experiments indicate that this particular analytical balance, which has been in continuous use for three years, has a sensitivity of 104 deflection units, or 1/104 mg., or 9.6 micrograms, with no load, and that the weighings of a sample on this balance can be reproduced to within ± 1 deflection unit, or ± 9.6 micrograms. Both sensitivity and precision of this balance remained practically unchanged at a 10-gram load (± 1 deflection unit; ± 9.7 micrograms).

ACTUAL WEIGHING

To permit equalization of possible temperature differences between the inside of the balance case and the balance room, the side doors of the balance are half opened about 10 minutes before weighing. For the same reason they should be opened again as soon as the actual weighing has been completed.

The object to be weighed is placed on the left-hand weighing pan (boat) or on the hooks of this pan (tubes). Whenever possible the object should be introduced through the side doors, both of which should

always be opened when this is done; objects which are placed on the hooks have to be introduced through the front. The counterpoise is then placed on the right-hand weighing pan and the doors of the balance are closed. After the rider has been placed on the 5-mg. mark the arresting mechanism is slowly released and the movement of the pointer observed. If the pointer swings to the right and beyond the scale, the balance is arrested and the rider moved to the 7.5-mg. notch. If, upon release of the arrestment, the pointer still swings too far to the right the rider is placed on the 10-mg. mark and the observation repeated; should the pointer still swing beyond the scale, then either a weight, such as the 10-mg. piece, is placed on the right-hand pan or the object is recounterpoised.

When, with the rider on the 5-mg. mark, the pointer swings to the left and off the pointer scale, then the rider is moved to 2.5 mg. and the observation repeated. If the pointer swings too far to the right, the rider is moved to a notch corresponding to half of the last two rider positions, in this case to 3.7 mg., and this division is continued until two limiting rider positions are found, one, the lower, when the pointer swings to the right, but no longer off the scale, and one, the higher, when the pointer, also remaining within the range of the scale divisions, swings to the left of the zero line of the pointer scale. Finally, a rider position which gives the smaller *deflection sum*, that is 50 or less, is chosen. On the ordinary analytical balance the rider is moved whole milligram divisions until the correct rider position is found.

After the *correct* position of the rider on the rider scale has been determined the average *deflection sum* is determined from three succeeding deflection sums, the balance being arrested after each determination of the deflection sum. The three *deflection sums* thus taken consecutively should agree within ± 2 or ± 3 deflection units on the micro-analytical balance and within ± 1 or at the most ± 2 deflection units on the analytical balance.

The *deflection sum* is added to the value of the beam reading if positive, or plus, and deducted from the beam reading if negative, or minus. Practical examples of such weighings performed on both balances are given below.

MICROANALYTICAL BALANCE

Series of Pointer Swings

| <i>First</i> | <i>Second</i> | <i>Third</i> |
|--------------|---------------|--------------|
| -16 + 59 | -7 + 51 | -20 + 61 |
| -10 | -1 | -13 |
| <hr/> | <hr/> | <hr/> |
| Average: -13 | -4 | -16 |

Deflection Sum

| | | |
|------------|------------|----------------------|
| +59 | +51 | +61 |
| <u>-13</u> | <u>- 4</u> | <u>-16</u> |
| +46 | +47 | +45 (Average = + 46) |

Actual Weight:

Position of the rider: 1.500 mg.

Deflection sum: 0.046

Weight: 1.546 mg. (1 deflection unit = 0.001 mg.)

ORDINARY ANALYTICAL BALANCE

Series of Pointer Swings

| <i>First</i> | <i>Second</i> | <i>Third</i> |
|--------------|---------------|--------------|
| -31 + 38 | -14 + 19 | -21 + 29 |
| <u>-29</u> | <u>-12</u> | <u>-20</u> |
| Average: -30 | -13 | -21 |

Deflection Sum

| | | |
|------------|------------|---------------------|
| +38 | +19 | +29 |
| <u>-30</u> | <u>-13</u> | <u>-21</u> |
| + 8 | + 6 | + 8 (Average = + 7) |

Actual Weight:

Position of the rider: 1.00 mg.

Deflection sum 7×0.0096 mg. 0.07 (1 deflection unit = 0.0096 mg.)

Weight: 1.07 mg.

Calibration of Weights

It is necessary to check the weight of the 10-mg., the two 20-mg., and the 50-mg. pieces against the rider, because they seldom are in absolute agreement with the weight they represent. Since they are placed on the right pan when used in an actual weighing, the weights must be calibrated under identical conditions. This is accomplished by employing the substitution method of T. W. Richards,^{16, 22, 26} which eliminates complicated calculations found in other procedures.^{8, 9, 15, 16, 18, 28, 29} Two sets of weights are necessary: set *W*, the weights to be calibrated, consisting of one 10-mg. (W_{10}), two 20-mg. (W_{20} and $W_{20'}$), and one 50-mg. piece (W_{50}); set *T*, the weights used as the tare, comprising one 10-mg. (T_{10}), one 20-mg. (T_{20}), and one 50-mg. piece (T_{50}).

The 10-mg. weight of set *T* (T_{10}) is placed on the left-hand pan,

while the rider is at the 10-mg. notch; readings are taken and the deflection sum (d_1) noted. Then the 10-mg. weight of set W (W_{10}), the weight to be calibrated, is placed on the right-hand pan and the rider moved to the zero notch; readings are again taken and the deflection sum (d_2) noted. The 10-mg. weight (T_{10}), which was used as the tare, is then replaced by the 20-mg. weight of set T (T_{20}); the calibrated 10-mg. weight (W_{10}) is placed on the right-hand pan and the rider inserted in the 10-mg. notch; readings are again taken. The 10-mg. weight is replaced by the 20-mg. weight of set W (W_{20}), the rider moved to zero, and the deflection sum noted. This procedure is repeated with the second 20-mg. weight of set W ($W_{20'}$). In calculating the results the corrected weight of the 10-mg. weight (W_{10}) has to be applied.

The calibration of the 50-mg. weight of set W (W_{50}) is carried out in the same manner, by placing the 50-mg. weight of set T (T_{50}) on the left-hand pan and the two 20-mg. weights of set W (W_{20} and $W_{20'}$) on the right-hand pan, while the rider is at 10 mg. The two weights on the right-hand pan are then replaced by the 50-mg. weight of set W (W_{50}) and the rider moved to the zero notch; again the corrected weight of the two 20-mg. weights has to be applied in the calculation. When the procedure of weighing has been completed, the results are tabulated as shown below and the correct weight of the pieces of set W calculated according to the following equation:

$$T = C + \frac{d_1}{1000} \quad T = W + \frac{d_2}{1000}$$

$$C + \frac{d_1}{1000} = W + \frac{d_2}{1000} \quad W = C + \frac{d_1 - d_2}{1000}$$

T = tare.

W = weight to be calibrated.

C = rider, or rider plus weight on right-hand pan when calibrating the larger weights.

d_1 = deflection sum with rider at 10.

d_2 = deflection sum with rider at 0 and weight to be calibrated on right-hand pan.

| | <i>Tare, mg.</i> | <i>Weight, mg.</i> | <i>Rider</i> | <i>Deflection Sum</i> | <i>Corrected Weight</i> |
|----|------------------|--------------------|--------------|-----------------------|-------------------------|
| I. | 10.000 | No weight | 10 | -31 | |
| | 10.000 | 10.000 | 0 | -36 | W_{10} 10.005 mg. |

$$W = 10.000 + \left(\frac{-31 + 36}{1000} \right) = 10.000 + \frac{5}{1000} = 10.005$$

| | | | | | |
|-----|--------|--------|----|-----|---------------------|
| II. | 20.000 | 10.005 | 10 | -26 | |
| | 20.000 | 20.000 | 0 | -14 | W_{20} 19.993 mg. |

$$W = 20.005 + \left(\frac{-26 + 14}{1000} \right) = 20.005 - \frac{12}{1000} = 19.993$$

| | <i>Tare, mg.</i> | <i>Weight, mg.</i> | <i>Rider</i> | <i>Deflection</i> | <i>Sum</i> | <i>Corrected Weight</i> |
|------|------------------|--------------------|--------------|-------------------|------------|-------------------------|
| III. | 20.000 | 10.005 | 10 | +18 | | |
| | 20.000 | 20.000' | 0 | + 8 | | W_{20}' 20.015 mg |

$$W = 20.005 + \left(\frac{+18 - 8}{1000} \right) = 20.005 + \frac{10}{1000} = 20.015$$

| | | | | | | |
|-----|--------|--------|----|-----|--|---------------------|
| IV. | | 19.993 | | | | |
| | | 20.015 | | | | |
| | 50.000 | 40.008 | 10 | +12 | | |
| | 50.000 | 50.000 | 0 | +20 | | W_{50} 50.000 mg. |

$$W = 50.008 + \left(\frac{+12 - 20}{1000} \right) = 50.008 - \frac{8}{1000} = 50.000$$

The accuracy of the aforementioned weights should be tested occasionally, and if their weight has increased materially they ought to be cleaned by washing with water and alcohol and polishing with a fine cloth. The weights should be handled only with the ivory-tipped forceps and kept in the balance case in a small dish lined with chamois. The rider may also change its weight; in this event the rider is washed in dilute potassium cyanide solution, dried, and gently rubbed between chamois-covered finger tips. Most of the time an increase in weight is observed; a decrease in weight occurs very seldom unless the rider is subjected to improper handling such as touching it with metal forceps; then it is best to replace it with a new one. Should the rider become bent, its shape may be restored by pressing it between several sheets of smooth, hard paper.

Preparation of Counterpoises

Since in quantitative analysis it is necessary to know only the weight of the sample and the weight of the reaction products, the weighing vessels are suitably counterpoised. The type of counterpoise varies with the type of weighing vessel used.

Theoretically, in order to minimize the buoyant effect of the air, the counterpoise should be of the same density as the object—metal for metal, glass for glass, porcelain for porcelain, etc.—and best also of the same shape and volume. Under adverse conditions the influence of variations in temperature and atmospheric pressure upon counterpoises may amount to as much as 20 to 40 micrograms.^{7-14, 25, 30} In practice, however, metal wire is used for light objects, and especially designed glass containers, so-called tare bottles, preferably provided with a ground-glass stopper and filled with lead shot or glass rods, are used for heavier objects.

The counterpoise for light objects is made of a paper clip or any corrosion-resistant wire. The first adjustment is made on an ordinary analytical balance by clipping or filing off portions of the wire until it is about 1 mg. *heavier* than the object; then it is placed on the micro-analytical balance and portions filed off until the counterpoise is about 1 mg. *lighter* than the object. The procedure for counterpoising with tare bottles is similar. The object is counterpoised on an ordinary analytical balance by adding lead shot to the tare bottle until it is about 10 mg. *lighter* than the object. For the final adjustment two sizes of lead shot are used, medium and fine, a single piece weighing approximately 10 or 5 mg., respectively. After the tare and object have been placed on the microanalytical balance a single medium-size lead shot is put beside the tare on the right-hand pan and the reading taken; lead shot is then added piece by piece until the bottle is about 1 mg. lighter than the object. The single lead shot which has been placed beside the tare bottle is then placed in the tare bottle. The properly marked counterpoises are kept in the balance case.

Numerous weighing procedures^{4, 6, 11, 19, 27} have been described in the literature,^{3, 7, 17, 18, 21, 23, 24, 25} as well as precautions to be observed when weighing on supersensitive balances. F. Breuer⁵ advised the use of crucible tongs for the placing of objects on the balance, as well as elongation of the rider rod.

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WEIGHING EQUIPMENT

The weighing equipment listed below is the *minimum* necessary and may be augmented by any of the many mechanical contrivances and gadgets already reported in the literature which fulfill similar purposes and which lend themselves to almost endless variations in design.

Forceps. Two kinds of forceps are needed. Forceps for handling the platinum boat and platinum foil should be all metal, of stainless steel; platinum tips are preferable but not absolutely essential. The second type is required for the handling of the weights. For this purpose ivory-tipped forceps which are furnished with each set of weights are in vogue. For a similar purpose and for handling capillaries, weighing tubes, weighing bottles, tares, etc., chamois-tipped forceps prepared as follows are recommended:³ A pair of metal forceps is heated in the flame of a Bunsen burner and some Krönig's glass cement is applied to the tips, which must be hot enough so that the glass cement remains molten while a small piece of chamois is attached to the inside. The superfluous chamois is cut off.

For the manipulation of larger objects ordinary crucible tongs with or without platinum tips are used. To lessen temperature changes in the balance case when introducing objects, weighing tools with long handles have been suggested and have found practical application for working under adverse conditions.² A special type of forceps having tapered grooves at the tips has been found convenient for the handling of the various kinds of capillaries employed in quantitative organic microanalysis.¹

Spatula. A plain metal rod of stainless steel, aluminum, platinum, or nickel of about 16-cm. length and 3-mm. diameter, flattened out at one end, is very convenient. A biological dissecting knife having a blade of 4- to 5-mm. diameter may be employed for the same purpose.

Probing Wire. A steel wire of 0.7- to 0.8-mm. diameter with knurled ends, around which cotton is wound, is an excellent device for cleaning the capillary ends of the absorption tubes, weighing tubes, etc. A tooth-pick quite often fulfills the same purpose.

Camel's-Hair Brush. A small camel's-hair brush is very convenient for the removal of particles adhering to the outer surface of the weighing boat or weighing tube.

Desiccator. Of the several types of desiccators ^{4, 5, 6, 7} available the following (Fig. 3) appears to be the most practical: ⁸ A round aluminum block of 62-mm. diameter and 45 mm. in height, has on its upper surface a concentric ring 6 mm. in diameter and 5 mm. in height; a 50-ml. flat-bottom crystallizing dish of 56-mm. outer diameter and 38-mm. height fits into the outer periphery of this ring and serves as a cover. In its center the metal block has a flat-bottom conical cavity, 35 mm.

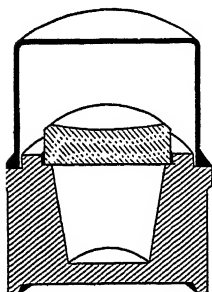


FIG. 3. Microdesiccator.

wide and 33 mm. deep, which serves as a convenient receptacle for crucibles used for the ignition of precipitates. The rim of this cavity is 5 mm. below the concentric ring and supports a concave copper block, of 39-mm. diameter and 12-mm. thickness, which serves as a support and efficient cooling device.

Platinum Wire. Platinum wire is bent at right angles at one end to form a small hook, the other end being fused into a glass rod of suitable length. The glass rod used for the introduction of platinum boats into the combustion tube is about 30 cm. long; the other for general use, such as cleaning of the platinum or porcelain boats, is about 20 cm. long, the wire for both being about 4 cm. long and 0.3 to 0.5 mm. in diameter.

Metal Tares. For counterpoising weighing boats and tubes, suitably bent rust-resistant wires are used. Ordinary paper clips have been found quite suitable for this purpose.

Tare Bottles. Tare bottles holding approximately 2 ml. for counterpoising absorption tubes, filter tubes, crucibles, etc., are approximately 18 to 20 mm. in diameter at the flat bottom and about 30 mm. in height with a neck 20 mm. in length and 6 mm. in diameter. Ordinary lead shot, as recommended by F. Pregl,⁶ may be used. The tare bottles are made of soft glass and provided with a ground-glass stopper. Pyrex glass, on account of its property to retain electrical charges, cannot be used for this purpose. Although the buoyant effect is not taken into consideration in counterpoises of this type, they nevertheless serve for all ordinary purposes. If possible, however, the counterpoise should be of the same material as the object, and various contrivances fulfilling this particular requirement have been described.^{9, 10, 11}

Rack. Since the absorption and filter tubes cannot be weighed immediately after their surface has been cleaned and wiped, a metal rack for their support should be included in the equipment. A pen-holder stand will serve this purpose very well. It is placed beside the balance on a piece of cardboard or notebook, because the temperature

of the stone or metal table top usually differs from the temperature prevailing in the balance case, thereby adversely affecting the constancy of weight of the object. It is also advisable to ground the rack to permit the electrostatic charges which are produced by the wiping of the glass surface to dissipate.

Chamois, Flannel, Absorbent Cotton. Half a dozen pieces of chamois measuring 10 by 10 cm. should be available for cleaning the balance, wiping the absorption and filter tubes, handling the weighing tubes and tare bottles, etc. The chamois should be frequently washed with soap and rinsed with dilute ammonia water and distilled water. They are dried at room temperature by suspending them from a glass rod or a string and when dry are rubbed to softness. For protection from dust they are placed in covered glass jars or Petri dishes. Extraction of the chamois with ether or chloroform should not be resorted to, because they usually become inflexible by this treatment. Moist flannel cloth measuring 10 by 10 cm. is needed to clean the surface of the absorption and filter tubes; fiber-free linen cloth may be used for the same purpose. Two sets of chamois finger cots for thumbs and index fingers facilitate the handling of all weighing vessels as well as the cleaning of the balance and should, therefore, be included in the equipment.

Ordinary non-medicated absorbent cotton is suitable for the various purposes mentioned in the following chapters.

Brushes. A large brush for the cleaning of the balance and a good small camel's-hair brush for brushing the platinum boat and weighing tube, etc., are required.

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LABORATORY UTENSILS

Microburners. It is necessary to have several microburners available, not only for the preparation of the capillaries, micropipets, and small glass rods, but also for various heating and drying purposes. The burner recommended by F. Pregl^{5, 12, 14, 17} is supported on four short legs and consists of a metal tube, one end of which is connected to a gas hose. Projecting at right angles from the side near the other end is a short gas jet with small air vents which take in sufficient air to give a nonluminous flame, which is reducible to a height of 3 mm. A screw controlling the flow of gas into the jet is inserted at this part of the metal tube. A vertical burner, incorporating the same principles, fulfills the purpose equally well, particularly if equipped with a needle valve. Several types of microburners are on the market, the most important feature of which is an exactly centered burner tip with sufficient but not too much air feeding. Microburners of Pyrex glass, of simple construction and easily made in the laboratory, work also well with natural gas⁷ and are widely used. They are made by drawing out a glass tube of approximately 7-mm. inside diameter to a capillary of about 1-mm. inside diameter which may be further reduced to suit specific purposes. The capillary end is bent at right angles and the feeding glass tube mounted on a cork of suitable size. Bunsen burners with a pilot flame arrangement are also sufficient for many purposes. A Venable type burner may be adapted to micro work by unscrewing the barrel and using the small gas outlet in the base.²

Gas Burners. Aside from the long gas burner shown in Fig. 20, a Méker burner, for the preparation of capillaries from test tubes, and a blast burner are required. For the movable gas burner employed in the various combustion procedures and referred to in this manual as *gas burner*, any standard gas burner such as a *Tirrill*, *Pittsburgh Universal*, *Venable* type, *Fletcher*, or *Bunsen* burner will be adequate.

Drying Blocks. A large variety of drying blocks have been designed and are described in the literature.^{2, 4, 10, 11, 12, 14} For the purpose of quantitative organic microanalysis the drying block of F. Pregl (Fig. 4),¹² which is used for the microvacuum desiccator and for drying of the filter tubes, has proved entirely satisfactory. It consists of two superimposed copper or aluminum blocks, each of which is provided with two

parallel semicircular channels. One of these channels, having a diameter of approximately 13 mm., serves to hold the center portion of the microvacuum desiccator or the halogen filter tube. The second channel has a diameter of approximately 8 mm. and can be used for various purposes. The lower half of the block is mounted on a solid base approximately 9 cm. in height and is heated from below by means of a microburner. It also has a horizontal boring which serves as a receptacle for the thermometer. The upper half of the block is removable and is provided with a heat-insulated handle. Two wires, suitably bent, extend from the base and are intended as supports for objects protruding from the channels.

Hand Centrifuge. An ordinary hand centrifuge, such as employed in clinical work, is wholly adequate for operations involving the centri-

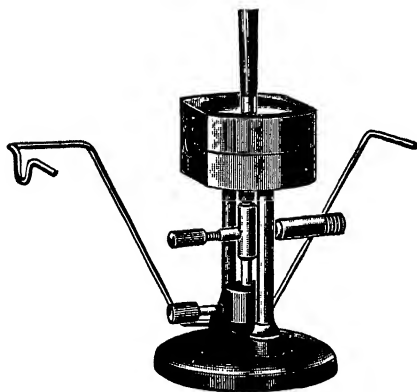


FIG. 4. Drying Block.

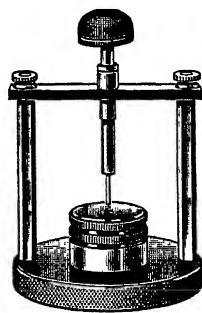


FIG. 5. Pellet Press

fuge cone, the filling of weighing capillaries, etc. The centrifuge cone is fitted into the larger metal tube by means of a suitably bored cork. The centrifuging of a capillary is best carried out by placing it in the centrifuge cone which has a protective cotton wad at the bottom to avoid breaking of the weighing capillary and which in turn is then inserted in the metal tube.

Pellet Press (Fig. 5). This apparatus¹² consists of a round, rust-proof, horizontal metal base plate about 8.5 cm. in diameter, 12 mm. in height and 6 mm. thick. It is provided with a polished surface and a vertical support 5.3 cm. high. The horizontal cross bar of this support is provided with a vertical support to act as a guide for the plunger or compressor. The base plate has a circular impression 0.5 mm. deep and 3.6 cm. in diameter, as a support for the bottom metal block, which

is 3.6 cm. in diameter and 1.5 cm. in height. This block has a cavity 2 cm. wide and 7 mm. deep in the center which serves as the receptacle for the finished pellet. The rim of this cavity is about 1 mm. lower than the edge of the base metal plate to support the cover block, which is 3.5 cm. wide and 1 cm. thick. A channel of 1-mm. bore is drilled through the center of the cover block through which passes the 12-mm.-long piston of the plunger. The substance to be compressed is introduced into this channel, and when filled it is pressed together by the plunger. During the process of the filling and pressing, the bottom block is placed upon the base in such a manner that its round cavity faces downward. A slight pressure is sufficient to form a coherent pellet 8 to 10 mg. in weight. In order to remove the pellet from the bore the position of the bottom block is reversed, so that in this instance the cavity faces the plunger. Re-insertion of the plunger into the bore of the upper block forces the pellet into the cavity of the bottom block. Then the pellet is cut into pieces weighing 3 to 5 mg., introduced into the weighing tube, weighed, and transferred to the reaction vessel. For reactive compounds, a pellet press made of glass¹³ has been recommended.

Glass-Cutting Devices. For cutting glass tubings a triangle file usually suffices. Capillaries, however, are most conveniently cut with the aid of ampule files. In the absence of such files, chips of glazed porcelain obtained from broken crucibles or evaporating dishes have proved themselves to be an entirely adequate substitute. Of lesser practical value are glass cutting knives or Carborundum stones, and the like.

Capillary Pipets. For the introduction or transfer of liquid samples or reagents, small micropipets are freshly prepared each time when needed. A piece of soft-glass tubing of 6-mm. outside diameter is held in the non-luminous flame of a Bunsen wing burner. When it softens it is removed from the flame and with a rotating movement drawn out to a capillary of 1-mm. bore. When cool it is cut off, and with the aid of a microburner the end is drawn out to a finer capillary of about 0.3-mm. bore. The finished pipet should be about 10 cm. long and taper down to about 1-mm. outside diameter. To prevent contamination of the sample with small fragments of glass, the end must be fire-polished by holding it briefly in a small flame and blowing air through at the same time, so that the walls do not collapse. A rubber bulb is placed over the wide end if necessary.⁴

*Precision Pipets.*¹² Such pipets are calibrated for 0.1, 0.2, 0.5 or 1 ml., and the manufacturers enclose a calibration certificate for capacity. Since the volume is known, the specific gravity of the liquid can be

determined with the same pipet. The inside diameter of the capillary at the tip and in the upper portion is sufficiently narrow to prevent the liquid from running out if the pipet is held in a vertical position. The pipet is filled by aspirating the liquid from a dish or beaker to just above the calibration mark. The pipet is then held in a horizontal position and any liquid on the outside of the conical tip is wiped off. A piece of filter paper is applied to the outlet and the excess liquid in the pipet is removed until the meniscus of the solution reaches the calibration mark in the stem. Should the mark be missed in withdrawing the excess, dipping of the pipet into the solution to be analyzed will fill it again, provided that the liquid has not receded into the bulb. The solution is transferred by blowing it out of the pipet, care being taken during this operation that the liquid does not spatter in the receptacle. To prevent contamination of the solution with saliva, a suitable rubber tubing with a glass mouthpiece, below which is placed a small cotton plug, is attached to the stem of the pipet. The outside of the pipet is rinsed with a few drops of distilled water while still held in the receptacle and then is refilled twice with distilled water; these washings are added to the sample solution. Pipets having a stem wide enough to permit the introduction of the wash liquid from the top have been found very convenient.

Similarly constructed pipets of 15-cm. total length with 0.5- and 0.1-ml. capacity respectively, but without the elongation in the upper stem and with a ground-glass cap at the tip of delivery stem, are used as standard pycnometers for taking the specific gravity of liquids.⁹

Centrifuge Cones. Centrifuge cones^{2, 4} of various sizes (2-, 1-, 0.5-ml., and less capacity), and made either of soft or hard glass or quartz, are used in a number of operations in quantitative organic microanalysis. Centrifuge cones with detachable ground-glass tips³ have been described and are used in a number of procedures. If loss of substance due to transfer to a standard weighing vessel has to be avoided, the small tip of the centrifuge cone is weighed together with the dry sample and introduced into the combustion apparatus, and at the end of the determination the cone is weighed back.

Wash Bottles. Various types have been described. The wash bottle found most satisfactory (Fig. 6) is of Pyrex glass and consists of a flat-bottom flask with a capacity of 250 and 150 ml., respectively.¹⁶ The head of the flask, which has a 19-mm. inner and 21-mm. outer diameter, carries a standard female ground-glass joint. The upper part of the wash bottle is provided with a standard male ground-glass joint, thus forming an outside glass-to-glass connection with the head, thereby lessening the danger of contaminating the wash liquid with the lubricant

or dirt. The two parts of the wash bottle are firmly held together by means of two wire springs attached to glass hooks fused to the head and neck of the flask. The delivery tube extends almost to the bottom of the stand flask, and its nozzle is drawn out to a capillary ending. The mouthpiece is provided with a saliva trap.

If the amount of wash liquid has to be measured, a graduated wash cylinder illustrated in Fig. 7 (Pyrex type 1112), of 50 ml. capacity and

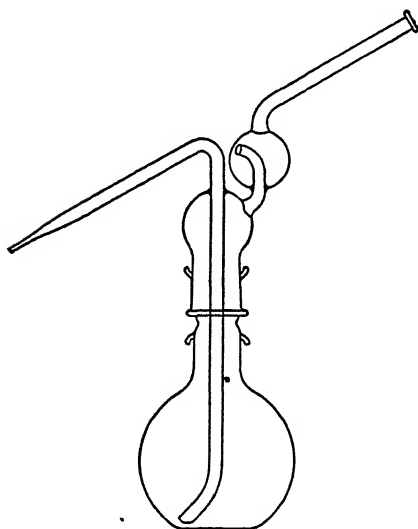


FIG. 6. Wash Bottle.

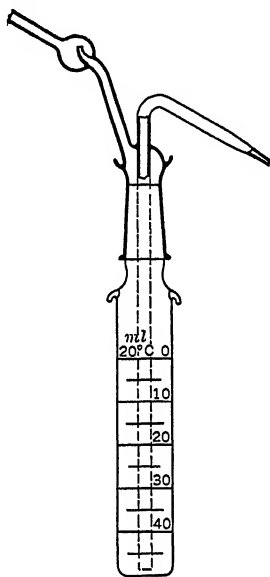


FIG. 7. Graduated Wash Cylinder.

with graduations of 1 ml., is very useful. This wash cylinder also is provided with an outside ground-glass joint and has a mouthpiece with a saliva trap like the wash bottle described above.

Miscellaneous. Other microanalytical laboratory utensils finding application in microanalytical procedures include a heating apparatus for the protective evaporation, or concentration, of solutions,⁶ removable burners,⁸ sublimation apparatus,¹⁴ glass knife sharpening blocks,¹ several stands serving as supports for the weighing tubes, etc., and other less common utensils.¹⁵

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PREPARATION AND WEIGHING OF A SAMPLE FOR ANALYSIS

General Directions

The object to be weighed must have the same temperature as the inside of the balance case. To attain this equilibrium it is placed beside the balance for 5 to 30 minutes before weighing, the time depending on its composition and size, as described. The side doors of the balance should remain open for at least 10 minutes before the weighing. Air currents inside the balance case, unequal temperatures due to body heat and breath of the operator, or adjacent warm objects may cause temperature changes which must be avoided. Smoking while weighing is absolutely fatal to accuracy. As a general rule it is advisable to keep away from the balance as much as possible between the actual weighings.

Sampling

Primarily, quantitative elementary organic microanalysis was developed for *homogeneous* and *pure* organic compounds, and this manual deals chiefly with such compounds. Micro samples of pure compounds taken for analysis are thus true representative samples of the substance to be analyzed. Hygroscopic substances, which tenaciously retain water or solvent, present a number of difficulties and have to be treated accordingly.

Occasionally it is necessary to obtain a representative micro sample from heterogeneous material. It may be a solution or a mechanical mixture. With solutions a thorough shaking is sufficient to secure a uniform aliquot portion of the substance. In a mechanical mixture, however, special sampling and grinding procedures have to be followed, a final particle size of 0.02 mm. being recommended.^{3, 4, 12, 15, 18, 19, 21, 32}

Weighing of the Sample

Weighing Boats. The boat, preferably of platinum, weighs approximately 0.6 to 1 gram and is 15 mm. long over all, 5 mm. wide, and 4 mm. high. Boats of porcelain, quartz, or hard glass are used, especially for the combustion of metal salts or if the substance has to be mixed with corrosive reagents.

The boat is cleaned by boiling it for a few seconds in a Pyrex test

tube with dilute nitric acid (1 : 1); most of the adhering acid is drained off by tilting it before it is taken out of the test tube; it is held with a platinum wire hook in the outer cone of a non-luminous flame of a gas burner until it glows bright red. The boat is then put on the metal block of the microdesiccator, which is placed beside the balance case. The platinum boat may be weighed immediately afterwards; porcelain, quartz, or hard-glass boats are allowed to stand for 10 minutes to establish temperature equilibrium. During the cleaning of the boat, the desiccator must be kept away from heat.

In the weighing procedure the boat is transferred to the left-hand pan of the balance with the ivory-tipped forceps, and the counterpoise is placed with the same forceps on the right-hand pan. The doors of the balance are then closed.

The boat is weighed as previously described on p. 26. After its weight has been determined, as represented by the beam reading, plus or minus the deflection sum, it is removed from the pan with the aid of the ivory-tipped forceps and placed on a clean surface such as the glass cover of the microdesiccator, or on a sheet of paper. Then the suitable amount* of substance is placed in the boat with the microspatula, and the boat, before being returned to the balance pan, is brushed in order to free it from particles of substance which might cling to its outer sides. The weight of the boat plus the sample is determined like the weight of the empty boat. By subtracting the weight of the empty boat from this result the weight of the sample is obtained. The boat containing the sample is then transferred to the microdesiccator where it remains until the beginning of the actual determination.

The weighing procedure described above should be completed within ten minutes, and since an appreciable change in the zero reading is unlikely to occur during this interval the zero reading need not be determined. But if the boat has to be weighed again after a greater lapse of time, then the zero reading must be determined before and after, and any changes should be taken into consideration and corrected for if they exceed the limits of the weighing error. When* weighing samples of 1 mg. or less, an unusually low amount, it is advisable to take the zero reading before and after each weighing and to calculate and apply a possible change according to the instructions given on p. 17. The same applies to oversensitive balances.⁶

* The amount of substance to be taken depends upon whether the micro or ordinary analytical balance is employed and to some extent also upon the particular determination, as well as upon the percentage element present in the compound. To be certain that the weighing error is well within the allowable experimental error the approximate amount required should be calculated beforehand. See p. 6.

Occasionally the sample has to be mixed with a solid oxidizing reagent, such as potassium bichromate for instance, which is used in the determination of carbon and hydrogen in organic salts, or with copper oxide if the compound is explosive or difficultly combustible. In this case the previously dried and finely powdered reagent is added to the weighed sample and mixed with it with the aid of a short platinum wire which is left in the boat during the course of the determination.

Weighing cups of tin or aluminum foil, which are made by taking a piece of foil 2 cm. square, folding it over the end of a glass rod 5 to 7 mm. in diameter, and then cutting it to a height of about 5 mm., find extensive application in a number of determinations.^{14, 23, 26, 34}

Weighing Tube (Fig. 8). This weighing tube, also referred to as charging tube,^{1, 9, 11, 16, 17, 24, 26, 35} is used whenever a solid substance is weighed which afterwards has to be transferred to another vessel

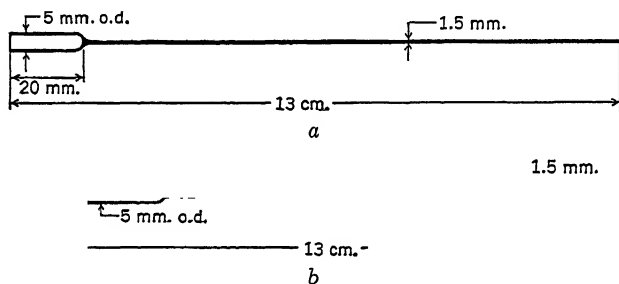


FIG. 8. *a*, Weighing Tube; *b*, Weighing Tube with Ground-Glass Cap.

such as an Erlenmeyer titration flask or a Kjeldahl digestion flask. It consists of a soft-glass tube of about 2-cm. length and 4-mm. inner diameter, to which is fused a glass rod about 11 cm. long and 1.5 mm. thick. It can be readily made in the laboratory by drawing out a soft-glass tube to a capillary of 4-mm. inner diameter, then drawing out this capillary once more in the flame of a microburner to a finer capillary, which is broken off 3 to 5 mm. beyond the constriction and fused to form a small knob. A glass rod about 1.5 mm. thick is sealed to this knob and cut to form a stem about 11 cm. long. The tube is cut to a length of 2 cm. and its mouth fire-polished, but without permitting its rim to curve inward. The weighing tube is counterpoised with a short glass rod in the following manner: A glass rod of about 4-mm. diameter is drawn out at one end to a thickness of about 1 mm. and the heavy part of the glass rod is cut off approximately 1 cm. beyond the beginning of the fine glass rod. The weighing tube is then placed on an analytical balance and small pieces from the thin end of the counterpoise are cut

off until its weight approaches that of the weighing tube but is still about 1 to 2 mg. greater. The final adjustment is carried out by placing the weighing tube on the hooks of the left pan and the counterpoise on the right pan and filing off the thick end of the counterpoise until it is approximately 1 mg. less than the weight of the tube. The blunt end of the counterpoise is then fire-polished, and what is left of the fine glass rod at the other end is bent by holding it in a flame, so that it will take a convenient shape enabling it to be held by the forceps when it is transferred to and from the balance.

In glass vessels, constancy of weight is somewhat more difficult to obtain and frequently can be achieved only after the glass object has been in the balance for ten or more minutes and until equilibrium in temperature has been reached.

The weighing tube is moved to and from the balance with the aid of a wire fork; before weighing it is wiped clean with a chamois and thereafter is handled only with protected fingers. The substance to be analyzed is introduced into the weighing tube with the microspatula, after which the surface and the orifice of the tube are brushed off. When the tube has been weighed it is removed from the hooks of the left-hand pan with the wire fork, grasped at its lower end with a chamois, and the contents emptied into whatever vessel is used for a particular determination. By tapping the stem of the weighing tube while it is inserted in the receptacle, most of the substance will be transferred. The tube, without brushing, is then weighed back. The weight of the substance is the difference between the two weighings.

Weighing Cups and Bottles. A variety of flat-bottomed weighing cups and bottles are used in quantitative organic microanalysis.^{8, 10} They may and often should be provided with ground-glass stoppers, and their size as well as shape are determined by the purpose which they serve. They are principally used to weigh very viscous, syrupy or hygroscopic liquids, or semi-solids subjected to the micro Carius halogen or sulfur determination and for some of the structure analytical methods such as the alkoxyl, alkimide, and acyl determinations.⁸

A variety of weighing capillaries are in use in quantitative micro-analytical work, depending on the method of analysis employed.

Capillaries for the Various Wet Combustion Methods. These are made of hard glass 1 to 1.5 mm. wide and 5 cm. long, open at both ends. They are weighed on a small support of metal sheet or wire.^{11, 26, 33, 35} The weighed capillary is dipped into the substance to be analyzed which has previously been placed on a glass slide. About 3 to 5 mg. of the liquid substance will thus enter the capillary. A solid sample is pressed into the capillary, or it may have to be pushed into it with a glass thread

fitting tightly into the bore. The capillary is brushed and wiped and placed on the balance pan so that the end containing the sample protrudes over the edge of the pan. After 5 minutes the weight of the capillary plus the sample is determined and the capillary dropped into the reaction vessel. This method of weighing has to be used for reactive substances or for semi-solids, waxes, oils, syrups, etc., which are to be subjected to wet combustion procedures (pp. 151, 182, 200).

*Capillaries for the Vaporimetric Molecular-Weight Determination*²⁹ (p. 221). Capillaries 8 to 9 cm. long and not less than 1.5 mm. in inside diameter are made from soft glass. They weigh about 150 to 200 mg. and are counterbalanced either by similar capillaries or by the weights and weighed as usual. The substance is melted on a microscope slide, on a small watch glass, or in a wider capillary. Then the weighed

d

FIG. 9. Weighing Pipet. *a*, Capillary Fused in the Center; *b*, Drawn out to a Glass Thread; *c*, Sealed at One End; *d*, Finished Weighing Pipet.

capillary is dipped into the melted substance which by capillary attraction is allowed to rise to a height of not more than 4 mm., thus giving an average sample of 3 to 6 mg. The capillary is then withdrawn and the sample allowed to cool and solidify. If solidification does not take place, a fragment of the original crystalline sample is brought in contact with the liquid to induce crystallization. The outside is again cleaned with a chamois, the capillary placed on the hooks of the left pan, and weighed after 5 minutes.

In addition to the aforementioned glass weighing vessels for solid substances, a number of modifications and combinations have been described.^{5, 7, 24, 30, 31} Any of these may be used or varied to suit individual requirements.

Weighing Pipets (Fig. 9).^{22, 26, 30} A soft-glass tubing of 6-mm. outside diameter is heated to its softening point in the non-luminous flame of a gas burner. Then it is removed from the flame and with a circular

movement around its axis it is drawn out to a capillary of 1-mm. bore, which is cut into pieces of 10-cm. length. The center of such a capillary is held in the flame of a microburner with constant turning until the walls collapse and form a solid thread which is drawn out to a diameter of about 0.5 mm. and to a length of approximately 3 cm. This thread is heated again in the center until it separates into two parts, thereby forming two capillaries, each possessing a convenient handle, the end of which is dipped into the flame until it forms a small knob. Since the capillary still is fully open at the other end, chemical reagents may now be introduced. For most combustion procedures, such as the determination of nitrogen by the Dumas method, the carbon-hydrogen, and in some of the other determinations, a few small crystals of anhydrous potassium chlorate are inserted in the capillary, centrifuged down to the sealed end, and fixed by fusion.

The capillary is then heated in the microflame approximately 10 mm. from the sealed end and drawn out to a fine capillary of 0.1-mm. bore, thus forming the bulb and the delivery stem of the weighing pipet. In the vaporimetric molecular-weight determination²² the bulb of the pipet is much shorter, only 3 to 5 mm., but its diameter is greater, about 2 mm. The fine delivery stem is cut to a length of 10 to 15 mm., care being taken at the same time that the capillary is open. It is advisable to prepare a number of such pipets at one time and keep them in a desiccator over a dehydrating agent.

The pipet is wiped before being weighed, is placed on the metal block of the microdesiccator, and after a few minutes its weight is determined. Then a small amount of the sample to be analyzed is placed on a slide or watch glass, the bulb of the capillary is gently warmed in the flame of a microburner, and the fine end of the delivery stem dipped quickly into the liquid. By subsequent cooling, a vacuum is created inside the bulb which causes the liquid to be drawn in. The droplet thus introduced is centrifuged to the bottom of the bulb so that as little substance as possible remains in the upper part of the pipet. Finally, the end of the delivery stem is sealed by holding it for a moment in the outer cone of a flame; the outside of the capillary is wiped clean and the pipet reweighed.

The above general procedures may be suitably modified; for very volatile liquids, for instance, the delivery stem of the pipet is made longer and finer, and the substance is sufficiently cooled prior to introduction into the pipet. For high-boiling liquids, the finished weighing pipets but with a wider delivery stem can be employed, or else the liquid may be introduced by means of another capillary before the stem is made, in which event the capillary delivery stem must be drawn out and sealed off without loss of glass.

For viscous and high-boiling liquids a *straight capillary* 9 to 10 cm. long is used. It is weighed as usual. One of its ends is dipped into the liquid, its outside wiped clean, and the capillary reweighed. It is cut about 2 mm. above the surface of the liquid and put into the reaction vessel or combustion tube. For low-melting solids such as fats and waxes, or for semi-solids, similar procedures may be employed (p. 46).

Many other weighing implements have been recommended for special applications, such as long capillaries of various diameters, combustion capillaries, etc.,^{5, 11, 26, 30, 35} as well as transfer capillaries or pipets of various lengths and diameters, but it is beyond the scope of this book to discuss them all in detail.

Hygroscopic Material

Although the many intricate devices and procedures adapted for the treatment of various hygroscopic substances^{2, 7, 11, 13, 20, 25-29, 31, 34, 35} cannot be taken up in detail, a few general procedures are given below which usually involve (a) the drying of the sample and (b) the protection of the dried material from atmospheric moisture during the weighing period.

Drying. For this purpose it is generally sufficient to place the substance in a vacuum desiccator containing appropriate drying agents—such as anhydron, concentrated sulfuric acid, phosphorus pentoxide—and resort to evacuation. Since the sample is small, the drying is, as a rule, quickly accomplished. The air entering the desiccator during the re-establishment of the normal pressure should be dried with the same drying agent.

For substances which have to be treated at higher temperatures but at normal pressure, the customary drying ovens will suffice; special metal blocks, heated with gas or electricity, are an added convenience.^{9, 11, 26}

Occasionally it is necessary to dry the sample at higher temperatures either at atmospheric or reduced pressure. Drying pistols of the usual design which may be evacuated and are charged with a drying agent serve this purpose very well.^{27, 34} A microvacuum desiccator as shown in Fig. 10^{9, 11, 26, 35} may also be employed; it consists of a glass tube 24 cm. long and 1 cm. in outside diameter, which is separated into two parts (a and b) by a capillary tubing 3 cm. long. The front section (b) is filled with anhydron; cotton wads are placed at both ends to prevent the capillaries from becoming clogged. Part (b) is closed with a perforated rubber stopper carrying capillary (c), which is connected to a bubble counter for the purpose of indicating a stoppage of the air current.⁷ The platinum or porcelain boat containing the sample is

placed in the drying chamber (a) which is closed with a drying tube (d) inserted in a rubber stopper. This drying tube has the same dimensions as (b) and is connected to a vacuum pump or water pump with a capillary tubing. After the minimum pressure has been obtained the entire desiccator is placed in the wide groove of the heating block, as shown in the illustration, and held in position by two cylindrical corks which are flattened at the bottom so that the apparatus can be placed on the table without rolling over and thereby spilling the sample. The block is

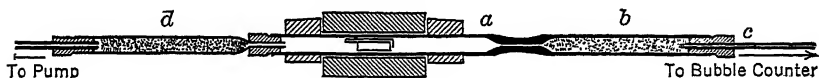


FIG. 10. Micro Vacuum Desiccator. Explanation in Text.

heated to about 70° C. for one-half to one hour, which usually suffices; then the desiccator is removed from the heating block and permitted to cool. The vacuum is broken gradually, and after the drying tube is detached the boat containing the substance is transferred immediately to the glass-stoppered *weighing piggy* described below and weighed.

Weighing.^{2, 11, 20, 25, 26, 28, 35} Only material which shows adequate constancy of weight, that is, agreement of several weighings within ± 5 micrograms, can be used for quantitative organic microanalysis if interpretability of the results is expected. The weighing of the previously dried material is best carried out in a *weighing piggy*,^{2, 22, 26} illustrated in Fig. 11. This device is equipped with a well-fitting ground-glass stopper provided with a long handle. The inside must be wide enough to permit the insertion of the boat; it rests on two short legs, and it has a glass handle at the end. Before being weighed it must be wiped with a chamois like the various other glass vessels described before. A weighing tube having a ground-glass cap may also be used for the weighing of hygroscopic substances.



FIG. 11. Weighing "Piggy."

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STANDARD SOLUTIONS

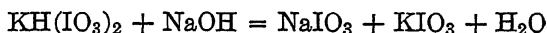
Principle

Three 0.01 *N* standard solutions are necessary:

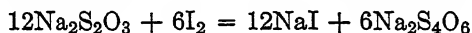
- 0.01 *N* potassium biiodate solution
- 0.01 *N* sodium hydroxide solution
- 0.01 *N* sodium thiosulfate solution

These solutions are sufficient for the procedures involving alkalimetric, acidimetric and iodometric titrations.^{9, 42} These titrations proceed according to the following equations:

(a) In alkalimetric and acidimetric titrations:



(b) In iodometric titrations:



Apparatus

Microburet (Fig. 12). The microburet consists of the vertical stem (a), the horizontal delivery tube (b), and the filling tube (c) which is provided with an automatic zero-point filling arrangement. The middle part consists of the calibration column (d), which is approximately 33 cm. long and has a capacity of 10 ml. with subdivisions of 0.05 ml. The lower part fits into a supply bottle of 1-liter capacity by means of a ground-glass joint and extends almost to the bottom of the supply bottle (e). Somewhat above the ground-glass joint a glass tube carrying a stopcock is sealed to the stem and a piece of rubber tubing which is dissected by a T-tube connects this glass tube to the pumping device (f). About 4 cm. above the ground-glass joint the vertical filling tube (c) branches off. On the opposite side of this tube is attached the nearly horizontal delivery tube (b) which extends approximately 10 cm. forward and then a short distance downward. To this end is attached a piece of good seamless rubber tubing 5 cm. long containing a glass bead which serves as a seal as well as a delivery valve when it is pressed

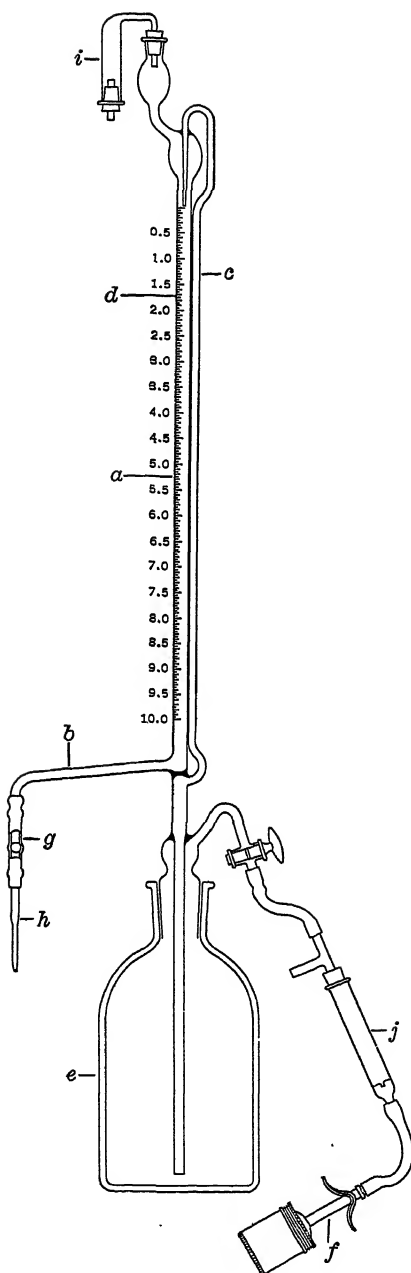


FIG. 12. Microburet.

with the fingers. To this rubber tubing (*g*) is connected the capillary delivery tube (*h*) which is approximately 7 cm. long and drawn out to a fine capillary ending of about 2-cm. length and a fine enough inner diameter at the tip to permit the withdrawal of drops measuring 0.01 ml.

To protect the solution from carbon dioxide, a safety tube (*i*), filled with Ascarite, is attached to the opening on top of the buret, and another safety tube (*j*), filled with the same reagent, is placed between the pumping device and the T-tube.

The buret as well as the supply bottle is cleaned by washing it repeatedly with cleaning solution, and then with ammonia and soap solution, after which it is exhaustively rinsed with distilled water. Before being filled the buret should be rinsed twice with small amounts of the respective standard solution.

Buret Stand. Although no specific device is necessary, the stand described below has proved to be a convenient arrangement.⁶ This stand has as a base a metal plate measuring 40 by 13.5 cm., on the four corners of which the vertical supports for the top plate are mounted. These supports are 11 cm. in height and 12 mm. in diameter. They are hollow and cylindrical in shape and support the top plate which is identical in dimensions to the base. The top plate has three circular

openings, 11 cm. in diameter, for the insertion of the supply bottles of three microburets. Held to the top plate by means of a vertical metal flap 5 mm. wide is the vertical front plate, measuring 40 by 10.5 cm. and made of white transparent glass. The horizontal frontal titration plate, measuring 40 by 9 cm., is made of the same material. Electric lighting units with *daylight* bulbs (blue, frosted lamps) are either built in between the burets or placed close to the burets by attaching them to the usual laboratory stand.

Dropping Bottles. Glass-stoppered dropping bottles of approximately 50-ml. capacity are used as containers for the indicator solutions.

Titration Flasks. Pyrex or quartz Erlenmeyer flasks of 25- and 50-ml. capacity are required; they must be steamed out before every titration.

Steaming Apparatus (Fig. 13). This apparatus consists of a round-bottomed Pyrex flask of 1-liter capacity. A conical glass funnel of 60° angle and having a diameter of 8.5 cm. at the rim is inserted into the neck of the flask by means of a one-hole rubber stopper. The stem of the funnel, 8 cm. long and 5 mm. in diameter, continues vertically up into the funnel for 12 cm. At its base the funnel is provided with a descending drain tube 4 cm. long and 6 mm. wide to which a rubber tubing of suitable length is attached to permit the condensing steam to drain into a sink. The steam which is generated in the round-bottomed flask passes through the funnel tube and by placing a titration flask over the funnel tube as shown in the illustration the flask is effectively treated with steam.

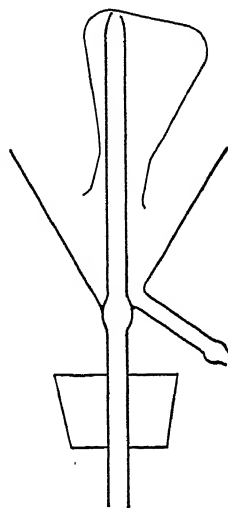


FIG. 13. Steaming Apparatus.

Reagents

Potassium Biiodate. Preparation: ⁴⁹ 110 grams of potassium chlorate is dissolved in 450 ml. of warm water and 40 ml. concentrated hydrochloric acid contained in a 2-liter Erlenmeyer flask which is placed in a well-ventilated hood. One hundred grams of powdered c.p. iodine is then added, and the reaction mixture is slowly warmed with occasional shaking until the reaction commences. The reaction proceeds rather violently with the evolution of chlorine, but if the heating is slight very little iodine is lost. After the reaction subsides the solution is boiled for a few minutes and filtered while hot. On cooling about 150 grams of biiodate crystallizes out, and this material is about 90%

pure. The crystals are filtered off by suction and are redissolved in 3 to 4 times their weight of boiling water, the resulting solution being filtered while still hot. After standing in the refrigerator over night the crop of crystals obtained is filtered off and dried at 100° C. in a drying oven for about one hour. The yield is about 100 grams of salt which is of sufficient purity.

Sodium Carbonate. Several grams of c.p. halogen and sulfate-free sodium carbonate is dried in a porcelain crucible at 300° C. for one hour with the thermometer in contact with the substance. Then, while still warm, the substance is transferred to a desiccator containing phosphorus pentoxide.

Sodium Hydroxide. C.P., in pellets or sticks.

Sodium Thiosulfate Pentahydrate (C.P. crystals).

Sodium Chloride. C.P. reagent quality.

Potassium Iodide Solution (4%). Four grams of potassium iodide c.p. is dissolved in 100 ml. of distilled water.

Hydrochloric Acid (sp. gr. 1.18).

*Sulfuric Acid*⁹ (Reagent quality). Ten per cent aqueous solution.

INDICATOR SOLUTIONS

Phenolphthalein. One per cent solution in 95% ethyl alcohol.

Methyl Red (0.3%). This solution is prepared by treating 0.15 gram of methyl red (*p*-dimethylaminoazobenzene-dicarboxylic acid) with 40 ml. of 0.01 *N* sodium hydroxide solution. The mixture is filtered and the filtrate stored in a glass-stoppered dropping bottle. The capillary of the glass stopper is drawn out to a solid glass rod of about 1-mm. thickness. Since only a trace of this indicator solution need be used, the glass rod is merely dipped into the indicator solution and some of it is transferred to the titration vessel by touching the inner wall. By tilting the titration flask the indicator is mixed with the solution to be titrated.

*Starch Solution*⁹ (1%). One gram of water-soluble starch is triturated with a few milliliters of cold distilled water, the resulting suspension is added to a boiling 20% aqueous salt solution, boiled for 5 minutes, allowed to cool, and then filtered. The filtered solution is transferred to a dropping bottle.

0.01 *N* POTASSIUM BIIODATE SOLUTION⁹

Preparation. 3.8994 grams of pure $\text{KH}(\text{IO}_3)_2$ is weighed on an ordinary analytical balance in a small porcelain dish which has previously been counterpoised and weighed. The substance is then transferred

to a 1-liter volumetric flask. To avoid loss of substance, it is best to place the porcelain dish containing the potassium biiodate in a wide funnel which is inserted into the neck of the volumetric flask. Hot distilled water is sprayed over the funnel and the substance, which thereby is washed into the volumetric flask. The empty dish is thoroughly rinsed, and the flask is filled to about three-fourths of its capacity with distilled water previously boiled to remove carbon dioxide. In order to dissolve the potassium biiodate completely, the flask may be heated on a steam bath. Thereafter the solution is cooled to the temperature at which the volumetric flask is calibrated and the flask filled up to the mark. Finally, the solution is transferred to the supply bottle of the microburet which previously has been cleaned as well as rinsed with two small portions of the solution.

Standardization. Although normally it is not necessary to standardize the solution when prepared as described above, its strength may be checked occasionally by titration with sodium carbonate as follows: A 3- to 5-mg. sample of pure sodium carbonate, previously dried at 300° C., is weighed in a stoppered weighing tube, transferred to a steamed-out 50-ml. Erlenmeyer flask, and dissolved in 5 ml. of distilled water. One drop of phenolphthalein solution is used as indicator, and the solution is kept at boiling temperature during the titration.

0.01 *N* HYDROCHLORIC ACID SOLUTION

This solution may be employed instead of the above potassium biiodate solution.

Preparation. There are several ways of preparing 0.01 *N* hydrochloric acid. One is by diluting a given volume (100 ml.) of 0.1 *N* hydrochloric acid with nine times its volume of carbon-dioxide-free distilled water (900 ml. to give 1 liter of 0.01 *N* hydrochloric acid) using a suitable (1-liter) volumetric flask. The 0.1 *N* hydrochloric acid solution may be prepared from redistilled concentrated hydrochloric acid in the usual manner, or by the use of Fixanal "Acid hydrochloric," which has proved entirely satisfactory. A tube of 0.1 *N* equivalent hydrochloric acid is pierced with the Fixanal standard piercing apparatus and the solution transferred quantitatively to a 1-liter volumetric flask. The transfer is accomplished by placing the delivery tube of the piercing apparatus which contains the glass nail in a ring clamp attached to a stand. The outlet of this delivery tube is inserted in the neck of the volumetric flask. Both are previously cleaned with cleaning solution and repeatedly rinsed with distilled water. The outside of the Fixanal tube is also rinsed repeatedly with distilled water. The tube is then thrown down into the delivery tube, so that the indentation at the

lower end is pierced by the glass nail of the piercing apparatus. The upper indentation is pierced with another glass nail and the inside of the Fixanal tube is rinsed profusely with distilled water, which is introduced through the upper opening.

For filling the volumetric flask as well as for the rinsing of the Fixanal tube distilled water is employed which is again boiled out shortly before being used. While permitted to cool, the flask is protected from the carbon dioxide in the air by an Ascarite tube. The solution is standardized in exactly the same manner as the potassium biiodate solution.

0.01 *N* SODIUM HYDROXIDE SOLUTION

*Preparation.*⁵⁰ A concentrated, carbonate-free solution is prepared by dissolving c.p. sodium hydroxide in an equal weight of distilled water in a rubber-stoppered flask which is placed on a water bath and kept at about 80° C. for twelve hours or at room temperature for at least a month. After this time any carbonate present will have precipitated out and settled to the bottom of the flask. One milliliter of the supernatant clear solution contains approximately 0.79 gram of sodium hydroxide. One half milliliter of this solution is added to 900 ml. of freshly boiled distilled water contained in a 1-liter volumetric flask. After thorough mixing, 5 ml. of this solution is withdrawn by means of a pipet and is titrated against the 0.01 *N* potassium biiodate solution using methyl red or phenolphthalein as the indicator. The additional volume of distilled water needed is calculated, but only 90% of the theoretical amount required is actually added. The titration and addition of distilled water are repeated until the strength of the sodium hydroxide solution is within 0.0101 and 0.0099 *N*. Then the solution is transferred to the supply bottle of the microburet.

Standardization. Seven to eight milliliters of the 0.01 *N* potassium biiodate solution, accurately measured, is run into an Erlenmeyer flask and a drop of phenolphthalein indicator solution is added. The solution is titrated with the sodium hydroxide solution, care being taken to remove any carbon dioxide from the titration solution by boiling it just before it turns alkaline. The titration is repeated using methyl red indicator solution. The end points obtained with the two above-mentioned indicators may differ slightly.

0.01 *N* SODIUM THIOSULFATE SOLUTION

Preparation. 2.48 grams of sodium thiosulfate pentahydrate crystals is weighed on an ordinary analytical balance and quantitatively transferred to a 1-liter volumetric flask, the procedure being similar to

the preparation of the 0.01 *N* potassium biiodate solution, but cold distilled water being used for rinsing. Next, 1.5 ml. of amyl alcohol is introduced and the flask is filled to the mark with distilled water. The solution is then ready for transference to the supply bottle of the microburet.

Standardization. The 0.01 *N* potassium biiodate solution becomes 0.12 *N* when reacting with potassium iodide in acid solution. Thus 0.7 to 0.8 ml. of the 0.01 *N* potassium biiodate solution is accurately measured with the microburet and run into a glass-stoppered 125-ml. Erlenmeyer flask. Three milliliters of 10% sulfuric acid⁹ in the cold, or concentrated hydrochloric acid with heating, and 2 ml. of the 4% potassium iodide solution are added. After the solution has stood for two minutes, titration with the sodium thiosulfate solution is begun. Before the complete disappearance of the iodine color the solution is diluted with 10 ml. of distilled water to about 20 ml. total volume; four or five drops of the starch indicator solution is then added and the titration stopped as soon as the blue color changes to a faint pink coloration.

Remarks

Standard Solutions and Indicators. The usability of the 0.01 *N* potassium biiodate solution in alkalimetric and acidimetric titrations encountered in quantitative organic microanalysis was investigated by J. B. Niederl and co-workers⁴² and for iodometric titrations by A. Elek.⁹ It was found that there was no interference (oxidation, etc.) when this reagent was used instead of the hydrochloric acid formerly employed. The use of solid samples of potassium biiodate in standardizations has long been established.^{9, 13, 28, 29, 49} Although this substance is in itself a standard, its 0.01 *N* solutions, which have proved to be very stable, may be checked in a similar manner as any other 0.01 *N* acid solution by titrating it with sodium carbonate^{35, 50} which has been dried according to G. Lunge.³⁹

The stability of the 0.01 *N* sodium hydroxide and the 0.01 *N* sodium thiosulfate solution has been repeatedly investigated,^{1, 2, 27, 30, 37, 42, 44, 46} and it has been found advisable to check the factor of the 0.01 *N* sodium thiosulfate solution at least once a week,¹⁶ while a monthly check of the 0.01 *N* sodium hydroxide solution is usually sufficient. For the stabilization of the sodium thiosulfate solution the addition of a small amount of amyl alcohol (0.15%) or of sodium carbonate (0.02%) has been found adequate.

The use of the three indicators, phenolphthalein for titrating organic acids with sodium hydroxide solution, methyl red for titrating ammo-

nium hydroxide solution, and soluble-starch solution for use in iodometric titrations, is well established. These indicators may be substituted by others having a similar pH range.

Microburets. Many types of microburets have been designed and many modifications have been devised.^{3, 4, 5, 17, 22, 31, 32, 40, 43, 51, 53, 54, 56, 58, 59, 60} Essentially any buret consists of three parts: the calibrated column, the outlet, and the filling device. Modifications in regard to the calibrated column are limited to the graduation employed. The burets used for titrations with 0.01 *N* solutions, as for the milligram processes employed in quantitative organic elementary analysis, are calibrated to 0.05 ml. for a total volume of 10 ml.^{13, 42, 44, 46} When finer graduation is necessary, the total capacity is smaller (2.5 ml.⁴⁰ and less). Under these conditions *syringe* burets are used.^{5, 7, 10, 26, 33, 36, 37, 45, 57} Such types of burets allow the withdrawal of as little as cubic millimeters and fractions thereof. These burets are usually operated with the aid of a mercury seal, the plunger being mounted on a drum with appropriate calibration. Some of these syringe burets even permit titrations on a microscope slide.²¹ Somewhat larger burets which are mounted vertically but operate without a mercury seal have also been constructed.⁴⁸

The outlet arrangement of a microburet consists essentially of the capillary tip and provisions for the withdrawal and stoppage of the titration fluid. This may be a rigid and permanent arrangement such as is found in all burets operated by means of a glass stopcock or a pinchcock which may be arranged vertically or horizontally.² The stopcock may be situated right below the vertical calibrated column,¹⁴ or it may, as is usual, be located at the delivery tube of the buret. For ease of operation without impairing precision, a glass bead is usually preferred, in which case the side arm of the buret is connected with the capillary tip by means of a rubber tubing. A glass bead is inserted in this rubber tubing which, when pressure is exerted upon the rubber tubing, allows the withdrawal of the solution in amounts small enough to be entirely satisfactory for microchemical practice. The titration flask can be held in one hand while the flow of the fluid is regulated with the other, and an interruption of the titration after withdrawal of each drop which occurs with glass stopcocks is avoided. Such an arrangement, furthermore, allows an easy exchange of the buret tips and of course eliminates the freezing-in of glass stopcocks, as well as clogging and contamination with stopcock grease. Burets with stopcock arrangements both at the top³⁸ and in the back, or provided with friction capillaries, have been described, as well as burets without any stopcocks.^{19, 36, 52} One such vertical buret, with mercury acting as

both sealing and replacing liquid, has been devised for potentiometric titrations.¹¹ Precautions to be observed in calibrating microburets have been given by E. Schilow.⁴⁷

As mentioned above, exchangeable capillary tips are usually preferred.²³ They may be connected to the delivery tube with a short piece of rubber tubing, or may be attached to it by means of a ground-glass joint.²⁵ To lessen capillary attraction and adhesion of the droplets delivered, these capillary buret tips may be treated with a trace of paraffin.

Various refilling devices are known.^{16, 40} The one most widely used is the pumping arrangement.^{13, 42, 44, 46} By increasing the air pressure in the system, part of the solution in the supply bottle is forced through the vertical filling tube into the top portion of the buret, which may or may not carry an automatic zero-point adjustment. Usually it is not advisable to rely on an automatic zero-point arrangement on account of possible incomplete drainage and leakage. The filling tube is usually outside and back of the calibrated column of the buret.

Most burets designed for routine work are provided with an adequate supply bottle of sufficient capacity to cope with the particular needs. One-liter supply bottles are usually employed. The smaller burets, the syringe burets, etc., do not need a supply bottle; other burets may have special devices on the top to serve as a reservoir⁴¹ or overflow chamber⁴⁰ for refilling them; such devices operate on either the vacuum or pressure principle.

Finally, there exist combinations of macro and microburets,^{8, 15, 24, 60} as well as combinations of pipets with burets¹⁶ and double burets.^{12, 18} The macro-microburets^{8, 15, 24, 60} usually consist of two calibrated columns, one with a larger total capacity but subdivided only in cubic centimeters or multiples thereof, and a second one of lesser capacity with appropriate subdivisions to 0.05 ml. and less. They are connected to the same delivery tube by means of a two-way stopcock. A buret connected to several supply bottles containing different standard solutions also has been reported,^{19, 20} as well as burets with automatic (electromagnetic) stirring devices.³⁴ Conditions and arrangements of apparatus for titrations in vacuum⁵⁵ as well as for electrometric titrations³⁸ have been studied.

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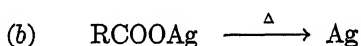
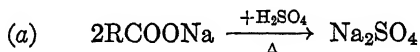
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ELEMENTARY ANALYSIS

I. DETERMINATION OF METALS

Principle

Metals in organic compounds are determined by combusting the substance in the presence of dilute sulfuric acid, or by simply burning off the organic constituents and weighing the remaining residue as sulfate (a), or metal (b).



Apparatus

The Micromuffle (Fig. 14). The micromuffle consists of two hard-glass tubes of Supramax or Pyrex glass 172. One is a horizontal com-

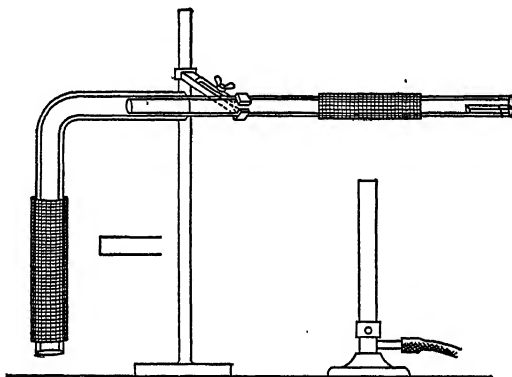


FIG. 14. Micromuffle.

bustion tube 18 to 20 cm. long and at least 8 mm. in inside diameter; the other is a rectangular tube, the vertical arm of which is approximately 15 cm. long and the horizontal arm about 8 cm. long and wide enough to permit the insertion of the horizontal combustion tube. A layer of asbestos paper is placed between the two tubes to provide a

well-fitting connection and to prevent them from cracking when heated. Both tubes may be heated by either Bunsen burners or electrical heating units. Wire gauzes of nichrome wire should be used for the protection of the combustion tube. The vertical tube is heated to supply a hot air current for the combustion and to facilitate the evaporation of volatile pyrolysis products. Electrical heating units offer the advantage of a more efficient and equal distribution of heat during the combustion, thereby preventing the substance from creeping over the boat. Their temperature should be regulated to be between 600 and 700° C.

Platinum Cylinder. To prevent the loss of substance because of its tendency to froth and spatter during the combustion, a platinum cylinder is used as a protective covering for the boat. This cylinder is made of platinum foil 0.04 mm. thick, is 3 cm. long, and has a diameter of 7.5 cm., i.e., a little less than that of the horizontal tube of the micro-muffle. A thin platinum wire about 2 cm. long is welded to the cylinder and the end of the wire is bent to form a hook which facilitates the manipulation of the cylinder.

Reagents

Sulfuric Acid (sp. gr.: 1.84). Diluted 1 : 5 with distilled water.

Nitric Acid (sp. gr.: 1.42). Diluted 1 : 1 with distilled water.

Procedure

The amount of substance to be taken depends upon the balance on which it is weighed; thus 3 to 5 mg. is taken if a microanalytical balance is employed or about twice as much if an ordinary analytical balance is used. The zero reading of the balance is determined first, and then the previously cleaned platinum cylinder and boat are weighed against a counterpoise, after which the required amount of substance is placed in the boat and both weighed again. The boat is placed on the glass cover of the microdesiccator and one or two drops of dilute sulfuric acid is added to the sample with a capillary. The boat is inserted in the platinum cylinder and both are placed far enough inside the horizontal combustion tube so that only the hook of the platinum wire protrudes from the opening. Heating is started with a slightly hissing flame approximately 5 cm. from the platinum cylinder and the burner is gradually moved toward the cylinder until it is reached, an operation which requires about 5 minutes. When no more fumes are given off the burner is placed directly under the cylinder and the heating continued with a somewhat stronger flame for ten minutes. Then, with the boat left inside the platinum cylinder, both are removed from the

combustion tube with steel or platinum-tipped forceps, held in the outer cone of a non-luminous flame until dark red, placed on the metal block of the microdesiccator, and weighed after five minutes. During these five minutes while boat and cylinder are permitted to cool, the zero reading of the balance should be determined so that any deviation can be corrected for. Should the residue show black particles, thus indicating incomplete combustion, another drop of dilute sulfuric acid is added and the combustion repeated, but the combustion tube is permitted to cool before both platinum cylinder and boat are introduced.

This determination may also be carried out without the platinum cylinder. The procedure remains the same, except that the boat must be approached more slowly with the flame in order to reduce the creeping of the substance to a minimum. Caution must also be exercised in removing the boat from the combustion tube, lest particles which have crept over be scraped off and lost.

Time:

| | <i>Minutes</i> |
|--|----------------|
| Determination of the zero reading..... | 5 |
| Weighing of the boat..... | 5 |
| Weighing of the sample..... | 5 |
| Combustion..... | 15 |
| Determination of the zero reading..... | 5 |
| Weighing of the residue..... | 5 |
| Total..... | 40 |

Calculation:

Log of weight of sulfate or residue,*
 Plus log of factor,†
 Plus negative log of weight of sample;
 Antilog (numerus) of total = percentage of metal.

Remarks

This method is suitable for the determination of the following metals in organic compounds: barium, calcium; potassium, and sodium² as sulfates; silver (salts), gold (aurates), and platinum (platinates) as metals. The literature^{5, 9, 11, 12} also reports successful application of this method to cadmium, cesium, lead, lithium, magnesium, manganese, rubidium,¹² strontium, and zinc, which are determined as sulfates. With lead, dilute nitric acid must be added to prevent possible reduction. By simple combustion in a porcelain boat, possibly with the

* See p. 297.

† Silver, gold, and platinum, as metallic residues, require no factor.

addition of dilute nitric acid, aluminum (Al_2O_3), chromium (Cr_2O_3), copper (CuO), iron (Fe_2O_3), magnesium (MgO), molybdenum (MoO_3), silicon (SiO_2), and tin (SnO_2) may be determined as oxides. Nickel and cobalt are determined as metals;¹³ the combustion, however, is carried out in a stream of hydrogen.⁴ A considerable improvement is the use of a platinum cylinder as described first by H. I. Coombs³ and applied to this method by H. K. Alber.¹ Electric heating has been suggested by C. J. Rodden.¹⁰ An automatic apparatus has been described by A. R. Norton, G. L. Royer, and R. Koegel.⁸ Suitably constructed torsion microbalances⁶ might be used for routine as well as lecture demonstrations. Residue determinations on samples weighing only a few micrograms have been reported by E. Wiesenberger.¹⁴

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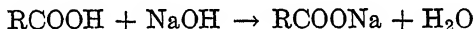
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II. DETERMINATION OF THE NEUTRALIZATION EQUIVALENT

IONIC HYDROGEN, CARBOXYL

Principle

The neutralization equivalent of an acid is the number expressing in grams the quantity of the compound required for the neutralization of 1 liter of normal alkali. For monobasic acids it is identical with the number representing the molecular weight; for polybasic acids it is a submultiple of this number.



On a microscale the method ^{6, 7} involves the titration of 4 to 8 mg. of an organic acid with standard 0.01 *N* sodium hydroxide solution while such factors as precaution against the absorption of carbon dioxide, the solubility of the acid, and the dissociation of the sodium salt are observed. To overcome the first, the solution is boiled near the end point; through the addition of ethyl alcohol the second and third are satisfactorily remedied.

Apparatus

Microburets, buret stand, titration flasks, dropping bottle, and steaming apparatus as described under *Standard Solutions* on pp. 51-61 are required.

Reagents

0.01 *N* Sodium Hydroxide Solution (p. 56).

0.01 *N* Potassium Biiodate Solution or 0.01 *N* Hydrochloric Acid Solution (p. 54).

Phenolphthalein Indicator Solution (p. 54).

Neutral Ethyl Alcohol (50%). One hundred milliliters of 95% ethyl alcohol is diluted with 100 ml. of distilled water; 2 to 4 drops of phenolphthalein indicator is added; the solution is boiled for about 30 seconds and then titrated to a slight pink coloration. The neutralization should be repeated from time to time.

Procedure

The substance is weighed in the weighing tube and transferred to a clean and steamed-out, but cool, Erlenmeyer flask of 50-ml. capacity. The substance is dissolved in 5 ml. of 50% neutral ethyl alcohol, warmed if necessary to get the sample in solution, and then titrated with 0.01 *N* sodium hydroxide until the end point is almost reached, as observed when the pink coloration just barely disappears upon shaking. At this point the solution is boiled for about 20 seconds to expel any carbon dioxide absorbed from the air and then it is quickly titrated to the end point, which is reached when the pink coloration is permanent for about one minute. If the end point is passed, 0.01 *N* acid is added in slight excess, the solution boiled again for a few seconds and then titrated back. If the solutions are not exactly 0.01 *N*, their respective factors must be determined as previously described and the necessary corrections applied.

Time:

| | <i>Minutes</i> |
|---|----------------|
| Weighing the weighing tube with the sample..... | 5 |
| Weighing the empty weighing tube..... | 5 |
| Titration..... | 15 |
| Total | <u>25</u> |

Calculation:

Neutralization Equivalent:

Negative log of ml. 0.01 *N* NaOH used,

Plus log of weight of sample;

Antilog of total = neutralization equivalent, or $1, \frac{1}{2}, \frac{1}{3}$
of molecular weight.

Percentage of Carboxyl:

Log of ml. 0.01 *N* NaOH used,

Plus log of factor (65331),

Plus negative log of weight of sample;

Antilog of total = percentage of carboxyl.

Remarks

The foregoing method is generally applicable to non-amphoteric acids, some lactones and anhydrides, some polynitrophenols, and acidic esters. No reports are given in the literature concerning a satisfactory application of this method to neutral esters. Phenolphthalein is used as indicator, although any other indicator having a similar pH range can be substituted for it. Application of this method to the analysis of binary mixtures of benzene carboxylic acids was proved feasible by

W. R. Kirner.⁵ Conductometric titrations of organic acids on a micro-scale have been performed by M. Furter and H. Gubser.²

The above method can also be used for the titration of amino acids,^{1, 8, 9} as shown by W. Grassmann and W. Heyde.³

The weighed amino acid is placed in a glass-stoppered 1-ml. volumetric flask and is dissolved in a minimum of water. By means of calibrated capillary pipets this solution is transferred to a steamed-out titration flask. Two drops of a 0.1% alcoholic indicator solution of thymolphthalein is introduced, and 0.01 *N* alcoholic sodium hydroxide solution is added from the microburet until a distinct blue coloration is obtained.

An amount of absolute alcohol equivalent to 9 times the volume of the original solution of the amino acid is added with a 5-ml. pipet having 0.1-ml. graduations. Upon the addition of the absolute alcohol the blue coloration disappears, and more of the standard alcoholic sodium hydroxide solution is added until the blue coloration is again obtained.

After the determination, a blank titration with exactly the same volume of absolute alcohol as was taken for the dilution of the amino acid is carried out and the amount of 0.01 *N* alcoholic sodium hydroxide solution used is deducted from the volume of alkali required for the neutralization of the amino acid solution.

This method gives satisfactory results provided that the amino acid solution is not excessively diluted. For a 0.01 *N* dilution, 10 times the amount of alcohol has to be added; with greater dilutions the concentration of alcohol may be increased to 80%, which, according to L. J. Harries,⁴ is still sufficient to retard the hydrolysis of the sodium salt of the amino acid formed in the titration.

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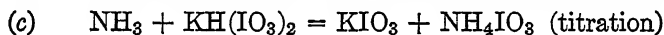
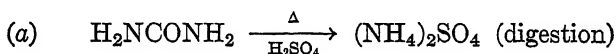
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III. VOLUMETRIC DETERMINATION OF AMINOID NITROGEN

KJELDAHL METHOD

Principle

The organic substance containing aminoid nitrogen is decomposed in the presence of concentrated sulfuric acid and suitable catalyzers to yield ammonium sulfate quantitatively.¹⁸ After liberation with strong alkali, the ammonia is distilled quantitatively into an excess of 0.01 *N* acid. The excess acid is titrated back with 0.01 *N* alkali. The reactions involved are as follows (using urea as an example):



Apparatus

*Distillation Apparatus*²⁸ (Fig. 15). A 1-liter round-bottomed Pyrex flask, two-thirds filled with distilled water, serves as a steam generator. Pieces of silicon carbide, or porous tile, or a trace of zinc dust is placed in the flask to insure even boiling. The steam generator is connected to the side arm of the cylindrical steam trap, which is provided with a drain arrangement at the bottom. A glass tube, bent at right angles at the top of this steam trap, forms a glass-to-glass connection of this part of the apparatus with the sealed-in steam delivery tube of the distilling flask. The steam delivery tube extends to the bottom of the distilling chamber and has an ascending side arm at the upper part, to which a small funnel of about 10-ml. capacity is attached with a short piece of rubber tubing carrying a pinch clamp. This funnel serves for the introduction of the digestion material into the distilling flask. The distilling flask proper is 30 to 35 cm. long and consists of a distilling or reaction chamber which widens at the top to a foam bulb; a second foam bulb, provided with a curved outlet tube, is sealed to the first. The distilling chamber is surrounded by a glass jacket, which is evacuated, thus eliminating the necessity of heating this part of the apparatus. The distilling

flask is held in an oblique position, so that the introduction tube leading into the distilling chamber is vertical. To lessen the danger of contamination of the distillate by the rubber connection, this outlet tube is attached directly to the short vertical arm of the silver tube condenser, which has an outside diameter of 7 mm. To make the glass-to-silver tube connection as tight as possible, the outlet tube should have the same outside diameter as the silver tube condenser. This part of the silver tube rises vertically for about 4 cm. and then ascends obliquely for a

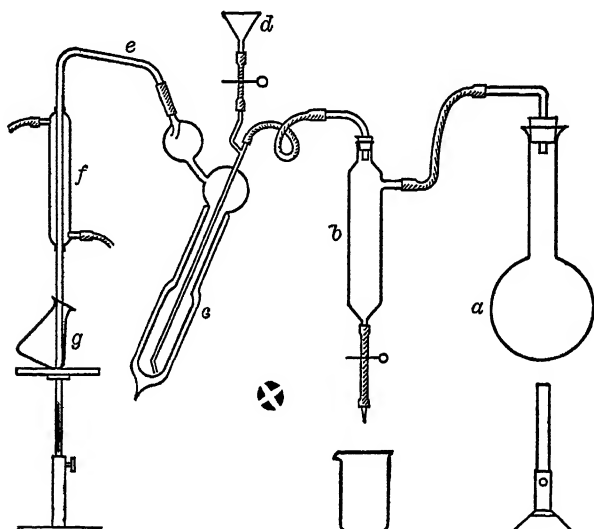


FIG. 15. Distillation Apparatus.²⁸ *a*, Steam Generator; *b*, Steam Trap; *c*, Distilling Flask; *d*, Introduction Funnel; *e*, Silver Tube Condenser; *f*, Condenser Jacket; *g*, Erlenmeyer Flask.

length of about 10 cm. and then is bent at right angles to descend vertically. A water-cooling jacket with a suitable water-trap funnel below, to prevent water from dripping into the Erlenmeyer flask, surrounds the lower part of the silver tube, which is about 35 cm. long. The end of the tube extends approximately 10 cm. beyond the cooling jacket and dips into the Erlenmeyer flask below.

Digestion Oven (Fig. 16). The digestion oven consists of a metal stand having an asbestos plate with six openings, covered with small round pieces of wire gauze. Centered below the openings and attached to the gas pipe of the stand are six microburners. The fume duct is approximately 42 cm. long and 4 cm. in diameter and is supported by two arms extending upward from the stand. It is connected to a

good water suction pump which effectively removes the decomposition vapors generated during the digestion. Electrically heated digestion ovens are also known.

Digestion Flask. Made of Pyrex glass 1 mm. thick, the digestion flask is about 16 cm. long with an outside diameter of 1.5 cm. at the

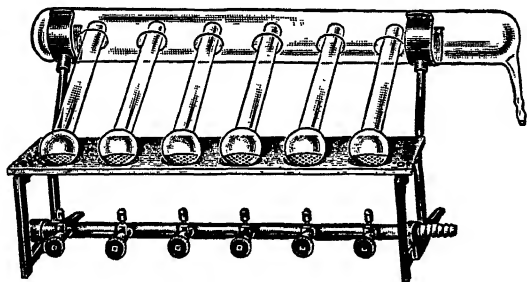


FIG. 16. Digestion Oven.

neck and has a bulb-shaped bottom of about 15-ml. capacity for the retention of the reaction material.

Titration Equipment. Titration equipment comprises microburets, buret stand, dropping bottle, titration flasks, and a steaming funnel and is described under "Standard Solutions" on p. 51.

Reagents

Concentrated Sulfuric Acid (sp. gr.: 1.84).

Catalyzers. A powdered, nitrogen-free mixture of 1 part potassium sulfate and 3 parts of copper sulfate;^{30, 32} powdered selenium;^{14, 19} mercuric acetate, or mercuric sulfate.^{26, 36}

Perhydrol. Nitrogen-free hydrogen peroxide, 30%.

Sodium Hydroxide Solution (30%). This solution is prepared by dissolving 240 grams of c.p. sodium hydroxide in 560 ml. of distilled water.

0.01 *N* Sodium Hydroxide Solution (p. 56).

0.01 *N* Acid Solution (potassium biiodate²⁵ or hydrochloric acid) (p. 54).

Methyl Red Indicator Solution (p. 54). This indicator solution is stored in a standard indicator bottle of about 50-ml. capacity, having a ground-glass stopper which is drawn out to a glass rod about 1 mm. thick so that no more than a trace of the solution can be taken at one time.

Procedure

Solids. The substance is weighed in the weighing tube and transferred to a clean, dry Kjeldahl digestion flask by holding the digestion flask in a horizontal position while introducing the weighing tube containing the sample. The digestion flask is then brought to a vertical position while the weighing tube is held as far as possible within the flask. By this manipulation most of the substance will fall directly into the bulb of the digestion flask and spilling of material on the wall of the neck of the flask will be avoided. The weighing tube is then withdrawn and weighed again.

Liquids. The liquid is weighed in a sealed capillary and placed in the digestion flask. After addition of the sulfuric acid the capillary is broken with a clean glass rod, which is rinsed with a few drops of sulfuric acid. For sticky syrups and heavy oils flat-bottomed weighing cups or bottles can be used.

Solutions. Solutions of liquids or solids, or biological material containing not more than 1 mg. of nitrogen per milliliter, are introduced into the digestion flask by means of a precision pipet of the weighing or wash-out type, which is provided with a rubber tubing ending in a mouthpiece of glass.^{30, 32} A small cotton wad is placed in this rubber tubing near the mouthpiece to prevent saliva from entering the pipet when its contents are being blown out. The pipet is rinsed once with the solution to be analyzed, then filled by drawing up the liquid to a few millimeters beyond the calibration mark. The tip of the pipet is wiped clean with a small cotton wad or filter paper, and, by still holding the pipet in a horizontal position and touching the tip with filter paper, the excess liquid is withdrawn. If the calibration is missed when withdrawing the excess, and provided that the level of the liquid has not receded into the bulb-shaped part, the pipet can readily be refilled by dipping it again into the solution. The measured portion is transferred to the digestion flask by holding the pipet as far inside the digestion flask as possible, without touching the side wall, however, and blowing out the contents. The tip of the pipet is rinsed with a few drops of distilled water from a wash bottle before it is withdrawn from the digestion flask. To complete the quantitative transfer of the solution the pipet is rinsed twice with distilled water and the washings transferred to the digestion flask in the same manner. Should bubbles form in the pipet, owing to improper manipulation in aspirating or blowing out the solution, the pipet is cleaned by rinsing it with ethyl alcohol and drying it on a suction pump.

Digestion. A knife point of selenium or potassium sulfate and cop-

per sulfate mixture is added to the sample in the digestion flask, and then 1 ml. of concentrated sulfuric acid is introduced which may be withdrawn from a macroburet set up for this purpose. The digestion flask is placed on the digestion oven and at first slowly, then vigorously, boiled until the contents have become perfectly clear and straw yellow or light green in color. Depending on the type of substance to be analyzed, fifteen to twenty minutes of boiling is generally sufficient; but if the digestion is still incomplete after this time, 2 to 3 drops of perhydrol is added to the digestion material and the heating continued for five to ten minutes. The last step may be repeated if the substance is extremely difficult to decompose.

Distillation. Approximately 7 ml. 0.01 *N* acid, accurately measured, is run from the buret into a 50-ml. steamed-out Erlenmeyer flask of Pyrex glass or quartz, to which a trace of methyl red indicator has been added. (Should the first distillation indicate that 7 ml. 0.01 *N* acid is not enough or much in excess, depending on the nitrogen content of the substance, correspondingly more or less 0.01 *N* acid is used for the following distillation; however, an excess of 1 to 2 ml. 0.01 *N* acid must be maintained.) Next, the cooled material in the digestion flask is diluted with 2 ml. of distilled water and cooled again under the tap.

With the water in the steam-generating flask boiling moderately, and the pinch clamp at the bottom of the steam trap open to provide an outlet for the steam, the contents of the digestion flask are quantitatively transferred to the distilling chamber of the apparatus by pouring the digestion material and two 2-ml. washings of distilled water into the small funnel on top of the distilling flask. This operation is aided by rinsing the mouth of the digestion flask with a few drops of distilled water from a wash bottle, or by making the outside of the rim of the digestion flask water-repellent through the application of a trace of stopcock grease. Then the Erlenmeyer flask containing the 0.01 *N* acid is placed under the silver tube condenser and raised until the tip of the tube dips well below the liquid. With the aid of a pipet 7 ml. of 30% sodium hydroxide is poured through the introduction funnel into the distilling chamber, which is sufficient to make the reaction material decidedly basic.

To begin with the distillation itself, the pinch clamp on the funnel and then the pinch clamp at the bottom of the steam trap are closed, forcing the steam to pass from the steam generator to the distilling flask. The duration of the distillation is exactly three minutes, counting from the time when the condensate enters the outlet tube of the second foam bulb of the distilling flask. After this time the Erlenmeyer flask is lowered until the tip of the silver tube condenser is about

1 cm. above the liquid, and the distillation continued for another minute. Before the Erlenmeyer flask is removed from the apparatus, the tip of the silver tube condenser is rinsed with a few drops of distilled water. Should the pink coloration of the liquid in the Erlenmeyer flask have become too faint, another trace of methyl red indicator may be added; but if the solution has turned yellow during the distillation, indicating the change from acid to alkali, the analysis must be considered spoiled because of the presence of insufficient 0.01 *N* acid to absorb quantitatively the ammonia distilling over. After the distillation the residue in the distilling chamber is automatically transferred to the steam trap by creating sufficient vacuum through the removal of the flame from under the steam generating flask. No further cleaning of the distilling flask is necessary, and the apparatus is ready for the next determination. The residue collected in the steam trap is drained off by opening the pinch clamp at the bottom.

Before starting a series of analyses, especially if the apparatus has not been in use for some time, it is necessary to steam out the entire system for about thirty minutes by closing first the pinch clamp at the bottom of the steam trap and five minutes later also the pinch clamp under the introduction funnel. An Erlenmeyer flask is placed under the silver tube condenser to receive the water distilling over. It is also advisable to test the apparatus as well as the purity of the reagents by a blank distillation. A properly set up and maintained apparatus and correctly prepared reagents should give no blank values.

Titration. The solution in the Erlenmeyer flask is boiled for about 20 seconds to expel carbon dioxide absorbed from the air and titrated to the end point with 0.01 *N* sodium hydroxide solution; the end point is reached when a canary-yellow coloration is obtained. If the 0.01 *N* solutions are not exactly 0.01 *N*, the respective factors must be determined as described on pp. 55-56 and the necessary corrections applied.

Time:

| | <i>Minutes</i> |
|--|----------------|
| Weighing or pipetting of the sample..... | 15 |
| Digestion..... | 20 |
| Distillation..... | 10 |
| Titration..... | 10 |
| Total..... | <u>55</u> |

Calculation:

Log of ml. of 0.01 *N* acid neutralized,
 Plus log of factor (14638),
 Plus negative log of weight of substance;
 Antilog of total = percentage of nitrogen.

Remarks

The volumetric determination of nitrogen by the Kjeldahl method^{18, 28, 29, 30, 32, 35} is generally applicable to substances containing aminoid nitrogen, which yield ammonia quantitatively during the digestion process. Thus the applicability of this procedure, without the introduction of reducing agents, is limited to amines, amino acids, ureas, thio ureas, and acid amides, provided that their structure is not too complex. Proteins yielding decomposition as well as hydrolysis products of a similar generic structure can also be determined by this method (factor: 6.25), as the wide application of this method in the analysis of biological or physiological fluids (urine, blood, etc.) indicates.^{1, 11, 39} It is suggested, however, that a test analysis of a known sample of the same or related structure be made first, or the determination be checked by a gasometric nitrogen (Dumas) determination.

Successful attempts to widen the applicability of this method by the introduction of reducing agents, such as reducing sugars (glucose) and hydriodic acid, have been reported by A. Elek and H. Sobotka,⁸ R. A. Harte,¹³ and A. Friedrich.¹¹ Their experimental findings illustrate the successful application of this method, with the appropriate modifications, to nitroso (β -nitrosonaphthol) and nitro compounds, aromatic amines, hydroxyl amines (oximes), hydrazines (substituted hydrazones, osazones), and some azo and diazo compounds.

For the reduction process with glucose the following quantities of reagents are employed: 3- to 10-mg. sample, 100 mg. glucose, 100 mg. potassium sulfate, 2 to 3 mg. copper sulfate or mercury or mercury acetate, 3 ml. concentrated sulfuric acid.

With hydriodic acid: 3- to 5-mg. sample, 1 ml. hydriodic acid (sp. gr.: 1.7), 2 to 3 mg. of red phosphorus and mercuric acetate, 100 mg. potassium sulfate.

The micro Kjeldahl method has been repeatedly discussed and its various phases scrutinized.^{2, 3, 21, 27, 34, 41} The discussion included: catalyzers, the sulfates of potassium,^{30, 32} copper,^{30, 32} mercury and mercuric oxide,^{26, 37} iron,²⁸ magnesium,³⁸ and selenium;^{14, 19} mixed indicators (methyl red and methylene blue, etc.);¹⁵ one-piece apparatus,^{4, 5, 10, 16, 17} of which the apparatus of P. L. Kirk¹⁷ has found the widest application.

This apparatus (Fig. 17) consists of a distillation flask *a* of 35-ml. capacity. This flask is inclosed in a glass jacket *b* which serves as a steam generator. A Y-shaped tube is sealed to the inner wall above the steam generator, one arm permitting the passage of steam from the steam generator and the other the introduction of the reaction

material through funnel *c*. Above the flask is a trap *d* and head leading to a condenser *e*, which drains through a vertical delivery tube into the receiver. An overflow and by-pass carry the water from the condenser water to the drain or to the steam generator, which is equipped with a drain tube. The total height of the apparatus is 35 cm. The steam generator jacket is 4.2 cm. in diameter and 16 cm. in height, the bulb being 6 cm. in diameter. The internal effective portion of the condenser is 1.8 cm. in diameter and 5.5 cm. in length.

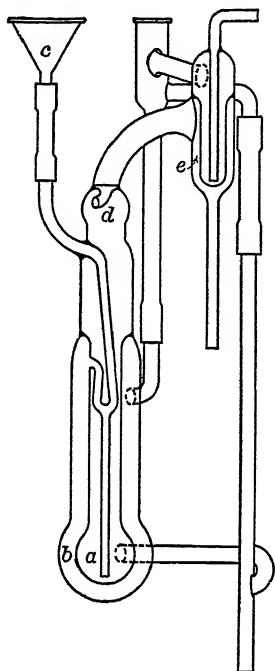


FIG. 17. One-Piece Distillation Apparatus.¹⁷ Explanation in Text.

Around the steam generator may be wrapped an insulating asbestos jacket to prevent sudden cooling from drafts. A few pieces of porous tile or silicon carbide are placed in the generator to prevent irregular boiling. A moderate flame should be used for the initial heating, and a strong flame as soon as the water begins to boil.

The use of the micro Kjeldahl method without a microanalytical balance^{14, 25} and the utilization of boric acid⁴⁰ in the titration for series determinations^{7, 20, 37} have been described, and adaptation to a semi-micro procedure (20–60 mg.)³¹ as well as for ultramicroanalysis (micrograms) have been reported.^{17, 23} Application of the micro Kjeldahl method to nitrogen determinations in coal³ and dyestuffs³³ as well as simultaneous determination of arsenic and chlorine⁵ have proved feasible.

An iodometric Kjeldahl method has been described by I. Bang¹ involving the iodometric determination of the residual free standard acid. This procedure is particularly applicable to substances with a low nitrogen content; the use of perhydrol and indicator, however, must be avoided. After distillation, the 0.01 *N* or 0.005 *N* acid is boiled for a few seconds to expel the carbon dioxide and then allowed to cool. Two to three milliliters of 5% potassium iodide and 1 ml. of 4% potassium iodate solution are added. After five minutes, during which time the solution is shaken repeatedly, the iodine is titrated with 0.01 *N* or 0.005 *N* sodium thiosulfate solution. A critical discussion of the iodometric nitrogen determination has been given by S. Morgulis and A. F. Friedman.²²

Of the other methods for the determination of aminoid nitrogen, the manometric method of D. D. Van Slyke,³⁹ which also has found extensive clinical use,^{6, 24} is the most important.

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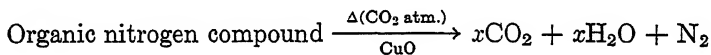
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IV. GASOMETRIC DETERMINATION OF NITROGEN

DUMAS METHOD

Principle

The gasometric determination of nitrogen by the Dumas method is applicable to any organic compound containing nitrogen in any form, such as amino, nitroso, nitro, azo, cyano, alkyl nitrites or nitrates, or heterocyclic nitrogen compounds. The substance is combusted in a closed system in an atmosphere of carbon dioxide; copper oxide is used as oxidizing agent, and metallic copper for the reduction of oxides of nitrogen to elementary nitrogen. To control the error due to the residual air in the carbon dioxide, which is determined separately in a blank determination, the combustion is carried out with a measured volume of carbon dioxide. The liberated nitrogen is collected quantitatively over 50% potassium hydroxide solution in a nitrometer.



Apparatus

Kipp Generators (Fig. 18, I and II). The Kipp gas generators I and II have a generating-chamber capacity of 2 liters and are connected, as shown in the illustration, by a glass tube carrying a three-way stopcock *A*, one arm of which is bent upward to extend above the marble in the generating chamber of Kipp I, while the other arm is connected to a glass tube leading into the top bulb of Kipp II. Another glass tube extends to the base of Kipp II and is bent at a right angle above the rubber stopper of the top bulb. The generating chamber of Kipp II has the same outlet arrangement as Kipp I, except that the three-way stopcock *B* is connected to the gasometer. Stopcock *A* serves for the deaeration of the generating chamber of Kipp I as well as for the evacuation of the top bulb of Kipp II. Stopcock *B*, aside from being used to deaerate the generating chamber of Kipp II, is also a safety stopcock to shut off the carbon dioxide in case of breakage of the glass tubing leading to the gasometer. Stopcocks *A* and *B* should have a minimum bore of 2 mm. to permit the ready flow of the carbon dioxide from one Kipp generator to the other.

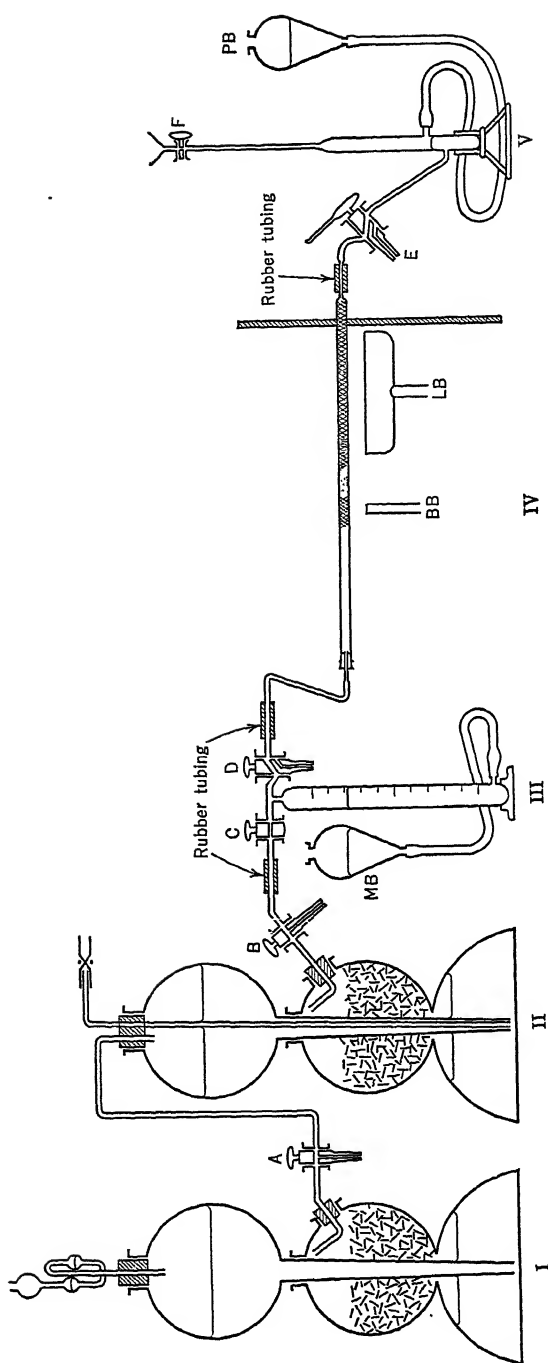


Fig. 18. Dumas Nitrogen Apparatus. I and II, Kipp Generators; III, Gasometer; IV, Combustion Tube; V, Nitrometer. A, B, C, D, E, F, Stopcocks; MB, Mercury Leveling Bulb; PB, Potassium Hydroxide Leveling Bulb; BB, Bunsen Burner; LB, Long Burner.

Preparation of the Kipp Generators. Because it is necessary to carry out the preparation of the Kipp generators within as short a time as possible, to prevent the prepared marble from absorbing air again, all glass tubes used for the various connections are previously cut to the right length, their ends are glazed, and the tubes bent to fit properly. Well-fitting rubber stoppers for the openings of the Kipp gas generators are also prepared and the glass tubes carrying the stopcocks inserted. With these preparations completed, Kipp generator I is put together, the ground-glass joint being well greased to form a perfect connection. Short glass rods, bent in V-form, are placed around the constriction between the middle and lower bulbs to prevent smaller pieces of marble from falling through. The generating chamber is filled to three-fourths of its capacity with marble, about 2 kg., and the side opening closed with a very tight-fitting rubber stopper carrying stopcock *A*, which is wired to this opening to withstand the pressure of the carbon dioxide. About 4 liters of hydrochloric acid is poured in, filling the bottom bulb up to the marble and the top bulb to one-half. To expel the air from the generating chamber carbon dioxide is generated repeatedly, but not too violently, by opening and closing stopcock *A*, thus bringing the hydrochloric acid in contact with the marble.

Kipp generator II, filled in the same manner, is then connected to the first, as shown in the illustration. Kipp I is closed at the top with a rubber stopper carrying a short-stem funnel tube with a double-loop trap containing mercury. The top bulb of Kipp II is closed by a two-hole rubber stopper through which extend two glass tubes; they are suitably bent as shown in Fig. 18. One glass tube extends to the base of the Kipp generator, and the other leads to the generating chamber of Kipp I. The former glass tube facilitates the convenient renewal of the hydrochloric acid, whenever necessary, without the necessity of disturbing the gas-tight connections of the apparatus. The outlet of this tube may either be sealed off or closed with a strong screw clamp. In order to retain a certain flexibility of the apparatus, thereby avoiding strain and possible breakage of the glass tubings, the various connections are not made glass-to-glass, but the ends of the glass tubings which are to be joined remain about 1 cm. apart, with the rubber tubings connecting them covering 2 to 3 cm. each of the two sections. To make all the rubber stoppers, rubber tubings, and the ground-glass joint between the top bulb and the generating chamber of the Kipp generator gas-tight, they are painted with Glyptal (No. 1201 red) or sealed with Picein. But considering that a properly set up apparatus will give an uninterrupted supply of very pure carbon dioxide for more than a thousand analyses, it is well worth the effort expended on the initial set-up.

With the gas-tight Kipp generators connected as shown in Fig. 18, both generating chambers should again be deaerated as previously described. To reduce the air content of the hydrochloric acid to a minimum, the top bulb of Kipp II is evacuated and the air replaced by carbon dioxide which is withdrawn from the generating chamber of Kipp I. This evacuation is carried out by attaching stopcock *A* by means of rubber tubing to a water-suction pump and turning the plug of the stopcock in such a way that Kipp I is shut off and the air withdrawn from the top bulb of Kipp II. Care must be exercised so that the hydrochloric acid in the bottom bulb does not recede below the wide tube of the Kipp generator. Stopcock *A* is then turned so that the carbon dioxide from the generating chamber of Kipp I fills the evacuated top bulb of Kipp II. By repeating this procedure of deaeration and evacuation several times in succession and again 24 hours later, the carbon dioxide supplied by Kipp II should be of sufficient purity to give satisfactory microbubbles. The purity of the carbon dioxide of a newly set up apparatus is tested by a blank determination as described on p. 94. Should the blank volume exceed the previously stated limits, then the process of deaeration and evacuation is repeated.

Microbubbles. Gas bubbles showing certain characteristics in speed and appearance when rising in the nitrometer are defined as microbubbles. Their characteristics are the following: They should require at least twenty seconds to rise from the surface of the mercury to the top of the nitrometer, be nearly absorbed by the 50% potassium hydroxide solution in the lower, wide part of the nitrometer, overtake each other in the stem, and ascend in a closely packed column. (With the set-up of the Kipp generators as described above, microbubbles showing these characteristics should be readily obtained.) According to F. Pregl the diameter of a microbubble should appear to measure 0.2 of a division of the nitrometer.^{43, 44, 47}

Gasometer (Fig. 19). In order to be able to measure the volume of carbon dioxide used for each analysis, a graduated gasometer of about 100-ml. capacity is inserted between Kipp II and the combustion tube. It rests on a grooved wooden block and is held in place by a clamp attached to a metal stand. The gasometer is made of thick-walled glass tubing, has a diameter of about 3 cm., and measures 30 cm. from the bottom to the capillary constriction leading to the T-shaped double stopcock arrangement. About 2.5 cm. from the bottom is an outlet which is connected to a mercury leveling bulb of about 400-ml. capacity by means of a securely fastened rubber tubing. To obtain the pressure necessary for the second phase of the combustion, the leveling bulb is placed in an open ring clamp, which is attached to the metal

APPARATUS

stand supporting the gasometer. The graduations reading from 0 to 100 ml., begin approximately 9 cm. from the bottom and are subdivided into divisions of 5 ml. The T-shaped arm of the gasometer carries two stopcocks about 5 cm. apart; a glass tubing of 8- to 10-mm. outside diameter and 2.5-mm. inside diameter extends 5 cm. beyond each stopcock. Stopcock *C*, having a plug with a one-way horizontal bore, intersects the glass tubing leading to Kipp II. The plug of the two-way stopcock *D* has an oblique bore which controls the connection leading to the combustion tube, and a downward outlet leading from the gasometer to the outside. This arrangement facilitates the regulation of the gas volume in the gasometer but forestalls the possibility of ruining an analysis by inadvertently turning the stopcock in the wrong direction. The gasometer is connected to the combustion train by a glass tube bent as shown in Fig. 18. The end facing the combustion tube is drawn out to a capillary and provided with a good rubber stopper which fits tightly into the mouth of the combustion tube.

Combustion Tube (Fig. 18, IV). The combustion tube is of hard glass (Pyrex 172) or quartz, the latter being preferred when substances have to be combusted at temperatures above 700° C. It is 52 to 54 cm. long and has an inside diameter of 8 mm. (± 0.5 mm.). The part facing the nitrometer ends in a capillary of 3-cm. length, 2-mm. inside and 3.25-mm. (± 0.25 mm.) outside diameter. The filling of the combustion tube consists of the *permanent* and the *temporary* filling. The permanent filling lasts for about 100 analyses, or until the copper oxide shows evidence of becoming reduced; the temporary filling is renewed for every determination. Before being filled the combustion tube is cleaned by

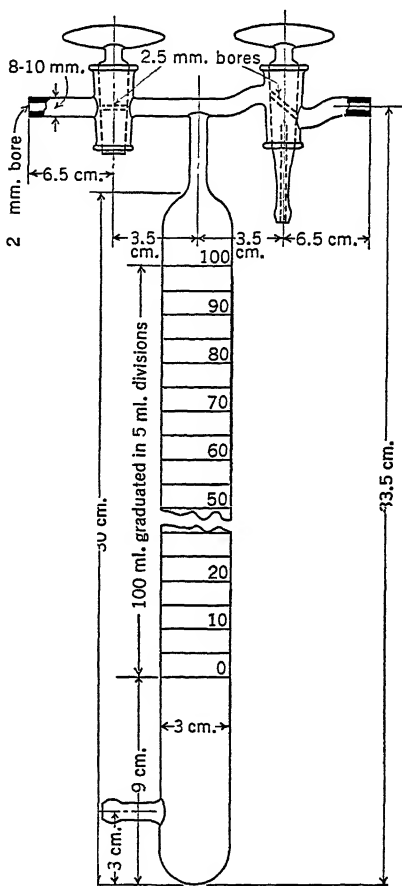


FIG. 19. Gasometer.

immersion for several hours in cleaning solution, kept for this purpose in a glass eudiometer tube about 50 cm. long and 2 to 3 cm. in inside diameter, then by exhaustive washing with tap water, distilled water and finally rinsing with ethyl alcohol. It is dried on the water suction pump, but its mouth is closed with a dust filter to keep the interior free from particles of dust. When clean and dry, the combustion tube is filled as follows: Pre-ignited asbestos is placed against the capillary constriction with the aid of a glass tube or wooden rod, and compressed to form a fairly compact plug 3 to 4 mm. thick. Coarse copper oxide, pre-ignited at 700°C ., or higher, is filled in to a length of 17 cm., the tube being tapped repeatedly during the process of filling so that the copper oxide forms a compact layer. Another asbestos plug 2 to 3 mm. thick is inserted, but not compressed too tight, and is followed by a 4-cm. layer of metallic copper wool or copper wire broken up into lengths

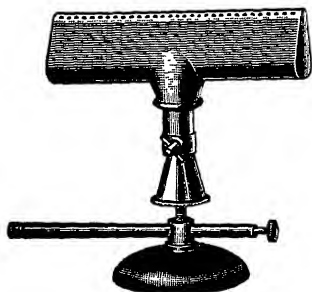


FIG. 20. Long Burner.



FIG. 21. Combustion Stand.

of 2 to 3 mm. Copper wool is usually preferred, because it provides a greater surface contact. A third asbestos plug, 3 to 4 mm. in length, concludes the permanent filling, which has a total length of 21 to 22 cm. The combustion tube is placed on the metal stand in such a way that the copper oxide filling facing the nitrometer extends 5 cm. beyond the stand, and the rest of the permanent filling, including the metallic copper layer, is completely within the range of the long burner or electric furnace, which should have an effective heating area 16 to 17 cm. long. After the permanent filling has been heated for about one hour in a slow stream of carbon dioxide, the combustion tube is ready for use.

Heating Unit. Either a gas burner or an electric heating unit ² may be employed. The long gas burner (Fig. 20) is approximately 17 cm. long and should be adjustable in height. Instead of this long burner, which consists of a flame distributor mounted on a gas burner, a detachable adapter, which serves equally well as a flame distributor and can be mounted on any gas burner (Bunsen or Tirrill), is entirely satisfactory.

The combustion stand (Fig. 21) ordinarily used in conjunction with the long burner is about 27 cm. long and 20 cm. high up to the V-shaped notches in the center brace at the ends of the stand. The two L-shaped side railings of the stand carry a separate U-shaped wire tunnel of the same length as the long burner to deflect the heat downward upon the combustion tube. The stand is also provided with a Transite plate which is riveted to an adjustable brace in front of the stand. For the movable burner a Bunsen or Tirrill burner is preferred. Another Transite or asbestos plate, 30 cm. high and 15 cm. wide and provided with an opening for the combustion tube, is fastened to the stand to protect the nitrometer from the heat emanating from the heating unit. If an electric heating unit is employed, the stand on which the combustion tube rests is usually an integral part of the furnace and consequently may vary in shape or construction, but essentially it should be similar to the stand described above.

Nitrometer (Fig. 22). The nitrometer or azotometer in which the nitrogen liberated during the combustion is collected and a separate two-way stopcock. Its measurements should closely conform to the specifications given in Fig. 22, because deviations invariably lead to difficulties and inaccuracies which may render the instrument practically worthless. The apparatus measures approximately 42 cm. over all; the upper, calibrated part is about

16 cm. long and has an outside diameter of 7 mm. and an inside diameter of 3.5 to 3.8 mm. The apparatus is calibrated for 1.5 ml. with graduations to 0.01 ml.; the 0.001 ml. are estimated with the aid of a suitable magnifying device attached to the stem of the instrument. It is very important that the buret of the nitrometer widen gradually to

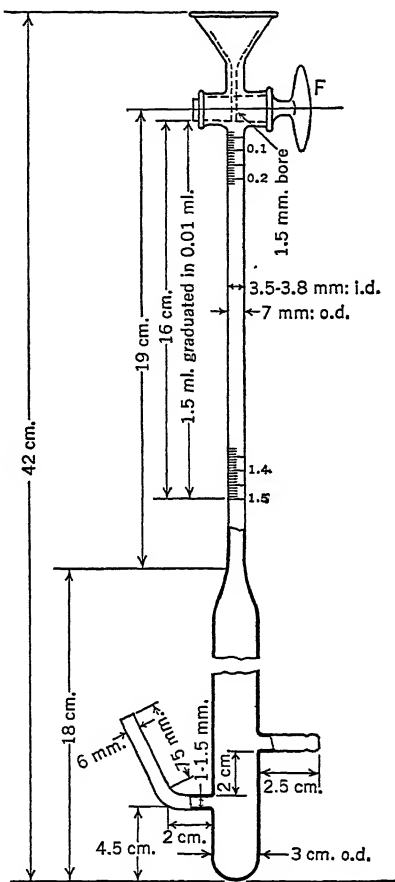


FIG. 22. Nitrometer.

the lower part like the neck of an Erlenmeyer flask to prevent the congestion of the gas bubbles at this point. This lower section of the nitrometer is about 18 cm. long and has a diameter of about 3 cm. Approximately 4 cm. from the bottom is a gas inlet, and 2 cm. above it on the opposite side is a side arm which is connected to the leveling bulb with alkali-resistant rubber tubing. The gas inlet tube enters the nitrometer horizontally, but ascends 2 cm. beyond at an angle of 45 degrees. Its inside diameter should be between 1 and 1.5 mm., but should not exceed 1.5 mm., because the size of the microbubbles and consequently also the duration of the combustion depend upon the inside diameter of this inlet tube. The two-way stopcock *E* (Fig. 23) is

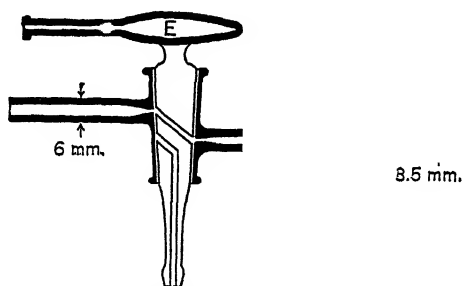


Fig. 23. Stopcock Leading from Combustion Tube to Nitrometer.

sealed to the nitrometer or attached with a heavy rubber tubing; the capillary outlet facing the combustion train is bent horizontally at the proper height to align with the capillary end of the combustion tube when the tube rests on the combustion stand. The stopcock has an oblique bore leading to the nitrometer and a downward outlet which permits the carbon dioxide to pass to the outside when sweeping out the air from the combustion tube before the combustion. Two fine grooves about 2 mm. long, etched into the end of the bore in opposite directions, permit a more accurate adjustment of the flow of the gases into the nitrometer.

Before being used and whenever necessary thereafter, the nitrometer is cleaned with cleaning solution, then rinsed well with tap water, distilled water, and alcohol, and placed upside down to dry. The stopcocks and rubber tubings, however, are removed and cleaned separately. The rubber tubing connecting the leveling bulb to the nitrometer is washed with 50% potassium hydroxide solution when necessary, and never with water. When clean and dry, the nitrometer is filled with mercury up to 1 mm. of the side arm which connects it with the leveling bulb by placing the mercury in the leveling bulb and letting it run

slowly into the nitrometer. The leveling bulb is filled with 50% potassium hydroxide solution to two-thirds of its capacity and placed in an open ring clamp at about the same height as the side arm. A ring clamp attached to a metal clamp holds the nitrometer loosely in place. Before the nitrometer is connected to the combustion tube with a rubber tubing of about 4-cm. length, 9-mm. outside diameter and 2-mm. bore, stopcock *E* is sparingly but nevertheless well lubricated with special stopcock grease.

Calibration Table. The calibration table expresses the correct volume to 0.001 ml. for every 0.01 ml. of the graduation of the nitrometer. It is usually supplied with every apparatus, but may also be made in the laboratory. Since the lowest point of the meniscus of the 50% potassium hydroxide solution is read, the calibration of the nitrometer with mercury must be carried out with the instrument in inverted position. Such measurements should be made for every 0.2 ml. beginning with 0.1 up to 0.9 ml., and for every 0.3 ml. thereafter. By interpolating the correct volume for each division (0.01 ml.) of the nitrometer, a chart may be prepared as shown in the table below, which illustrates

PRECISION NITROMETER ACCORDING TO F. PREGL, AT 20° C. (KOH)

| ml. | 0.00 | 0.01 | 0.02 | 0.03 | 0.04 | 0.05 | 0.06 | 0.07 | 0.08 | 0.09 |
|-----|-------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | Capacity in Milliliters | | | | | | | | | |
| 0.1 | 0.099 | 0.109 | 0.119 | 0.129 | 0.139 | 0.149 | 0.159 | 0.169 | 0.179 | 0.189 |
| 0.2 | 0.199 | 0.209 | 0.219 | 0.229 | 0.239 | 0.249 | 0.259 | 0.269 | 0.279 | 0.289 |
| 0.3 | 0.299 | 0.309 | 0.319 | 0.329 | 0.339 | 0.349 | 0.359 | 0.369 | 0.379 | 0.389 |
| 0.4 | 0.399 | 0.409 | 0.419 | 0.429 | 0.439 | 0.449 | 0.459 | 0.469 | 0.479 | 0.489 |
| 0.5 | 0.499 | 0.509 | 0.519 | 0.529 | 0.539 | 0.549 | 0.559 | 0.569 | 0.579 | 0.589 |
| 0.6 | 0.599 | 0.609 | 0.619 | 0.629 | 0.639 | 0.649 | 0.659 | 0.669 | 0.679 | 0.689 |
| 0.7 | 0.698 | 0.708 | 0.718 | 0.728 | 0.738 | 0.748 | 0.758 | 0.768 | 0.778 | 0.788 |
| 0.8 | 0.798 | 0.808 | 0.818 | 0.828 | 0.838 | 0.848 | 0.858 | 0.868 | 0.878 | 0.888 |
| 0.9 | 0.898 | 0.908 | 0.918 | 0.928 | 0.938 | 0.948 | 0.958 | 0.968 | 0.978 | 0.988 |
| 1.0 | 0.998 | 1.008 | 1.018 | 1.028 | 1.038 | 1.048 | 1.058 | 1.068 | 1.078 | 1.088 |
| 1.1 | 1.098 | 1.108 | 1.118 | 1.128 | 1.138 | 1.148 | 1.158 | 1.168 | 1.178 | 1.188 |
| 1.2 | 1.199 | 1.209 | 1.219 | 1.229 | 1.239 | 1.249 | 1.259 | 1.269 | 1.279 | 1.289 |
| 1.3 | 1.299 | 1.309 | 1.319 | 1.329 | 1.339 | 1.349 | 1.359 | 1.369 | 1.379 | 1.389 |
| 1.4 | 1.399 | 1.409 | 1.419 | 1.429 | 1.439 | 1.449 | 1.459 | 1.469 | 1.479 | 1.489 |
| 1.5 | 1.499 | | | | | | | | | |

this type of calibration as recommended by F. Pregl.^{43, 44, 47} A graphical chart may also be employed. In such a chart the abscissa carries the milliliters (0.1 to 1.5 ml.), while the deviations in the graduation

form the ordinate. A nitrometer closely following the zero line would indicate perfection, and calibration errors that remain constant would disclose a satisfactory instrument, whereas a nitrometer showing a calibration curve changing repeatedly from plus to minus obviously would be of doubtful value.

Introduction Funnel. For the introduction of copper oxide and substance into the combustion tube a funnel is employed. It is made from a test tube, and its upper section is 4 to 5 cm. long and about 2 cm. in diameter; it is drawn out gradually to a conical capillary 6 to 7 cm. long and 3 to 4 mm. in diameter. This long stem is necessary to prevent particles of fine copper oxide, to which substance may adhere, from settling near the orifice of the combustion tube.

Reagents

Marble. Clean marble, about 2 kg. for each Kipp generator, is broken up into pieces small enough to pass through the side opening of the generating chamber. It is treated previous to its use by washing it with dilute hydrochloric acid (5%), decanting the solution, and then boiling the marble with water in a thick-walled flask for two to three hours, changing the water until it remains clear. To expel the air from the pores of the marble the flask is attached to a water suction pump and evacuated for about thirty minutes; this procedure of boiling and evacuation may be repeated several times. To prevent the reabsorption of air the marble is kept under water until it is placed in the Kipp generator.

Hydrochloric Acid. Four volumes of concentrated hydrochloric acid (sp. gr.: 1.178–1.185) are diluted with one volume of distilled water. About 4 liters of this diluted acid is required for one Kipp generator.

Copper Oxide. Copper oxide in wire form is used; it is 3 to 5 mm. long and about 0.5 in diameter and should be without pores. Porous copper oxide, because of its tendency to retain air, is objectionable; after pre-ignition it should be evacuated in a side-arm test tube and then saturated with carbon dioxide. The fine copper oxide, of 40 to 100 mesh, is obtained by grinding the copper oxide wires and sifting through sieves of 40 to 100 mesh. Both forms of copper oxide are used over again after being re-ignited separately in a nickel or iron dish over a blast flame at 700 to 800° C., or being heated to a dull red for fifteen minutes. Coarse and fine copper oxide are kept in separate test tubes of about 80-ml. capacity, preferably in an atmosphere of carbon dioxide.

Metallic Copper. Copper wool or copper in wire form serves this purpose. Copper wool, pressed to form a roll about 4 cm. long and of somewhat smaller diameter than the inside diameter of the combustion tube, is effectively reduced by igniting it and placing it, while still hot, in a test tube containing a few milliliters of methyl alcohol. The copper wire is reduced by heating it in an atmosphere of hydrogen.

Mercury. Clean mercury is used for the safety funnel tube of Kipp generator I, for the leveling bulb of the gasometer, and as a sealing liquid in the nitrometer. About 3.5 kg. is needed in all.

Potassium Hydroxide Solution (50%). Potassium hydroxide (c.p. in pellets) is dissolved in an equal weight of distilled water. It is left standing for 24 hours and then is filtered through good fluted filter paper, glass wool, or a Büchner funnel covered with Gooch crucible asbestos. The filtration is repeated until a perfectly clear solution is obtained, which is stored in a rubber-stoppered reagent bottle.

Stopcock Grease. Heavy vaseline with a lanolin base is used as a lubricant for all the stopcocks of the apparatus.

Procedure

Solids. The finely powdered substance is weighed in the weighing tube and transferred to a mixing tube about 7.5 cm. long and 1 cm. in diameter. A Pyrex test tube having these dimensions, but without flare, will serve the purpose. Sufficient substance should be taken to obtain a volume of nitrogen amounting to at least 0.3 ml.

Liquids. The liquid sample is weighed in a sealed capillary pipet.¹⁴ After the introduction of the 5-cm. layer of coarse and the 2-cm. layer of fine copper oxide into the combustion tube, the capillary is centrifuged; its tip is then broken off, and the capillary and the tip are placed in the combustion tube with the open end of the capillary facing the temporary combustion-tube filling; more fine copper oxide is added until the capillary is completely covered.

Viscous oils, thick syrups, waxes, sticky semi-solids, and hygroscopic substances are weighed in a porcelain boat; the substance in the boat is covered with fine copper oxide and then placed in the combustion tube after the temporary combustion-tube filling. Sufficient fine copper oxide is added to cover the boat.

Introduction of the Temporary Filling and the Substance. The combustion tube is detached from the apparatus by first pulling out the gas inlet tube from the rubber stopper, removing the stopper, and then disconnecting the combustion tube from the nitrometer; the rubber con-

nection remains attached to the nitrometer. The temporary filling present is removed by tapping and placed in a wide-mouth reagent bottle. The combustion tube is wiped twice with a cotton wad wound tightly around the roughened end of a stiff iron wire about 40 cm. long. A 5-cm. layer of coarse copper oxide is introduced directly into the combustion tube and is followed by a 2-cm. layer of fine copper oxide which is added by means of the introduction funnel. This constitutes the *temporary* combustion-tube filling. A 2-cm. layer of fine copper oxide, or more for a sample exceeding 5 mg., is added to the substance in the mixing tube, which is tapped to free its mouth from particles of copper oxide, closed with a tight-fitting cork, and then well shaken to mix the substance thoroughly with copper oxide. By tapping the mixing tube, loosening the cork, and then tapping it again, the possibility of losing traces of substance adhering to the cork is prevented. The mixture of fine copper oxide and substance is transferred to the combustion tube with the aid of the introduction funnel. About 1 cm. of fine copper oxide is then placed in the mixing tube, which is again well shaken and the material transferred to the combustion tube as before. To insure the quantitative transfer of the substance this washing is repeated once more, whereupon the funnel as well as the combustion tube are repeatedly tapped to prevent particles of substance from remaining on the upper part of the combustion tube. Finally, a little coarse copper oxide, no more than enough to form a 1- to 1.5-cm. layer, is added directly to assure the accomplishment of this purpose.

Two wire gauzes 5 cm. long for the movable burner and one 19 to 20 cm. long for the long burner are placed over the combustion tube for its protection from the flames of the burners; they are slipped over the capillary ending of the combustion tube, with the long wire gauze covering the permanent filling. To keep the temporary filling from being spread in the combustion tube, it is brought into a vertical position, tapped, and then placed on the combustion stand. The mouth of the combustion tube and the capillary end are cleaned with cotton wound around a toothpick or the small knurled iron wire. The capillary ending, the rubber stopper, and the capillary of the glass tube leading to the gasometer are lubricated with a trace of glycerin. The rubber stopper is moistened very sparingly, because if excessively lubricated it may be forced out of the combustion tube when it is placed under pressure, thereby ruining an analysis. The combustion tube is attached to the apparatus by first connecting it glass-to-glass to the nitrometer, then inserting the rubber stopper and through it the capillary of the glass tube of the gasometer in such a way that the tip of the capillary projects not more than 1 mm. beyond the rubber stopper in the mouth of the

combustion tube. Finally, the combustion tube is so adjusted that it rests evenly on the combustion stand and the permanent filling at the capillary ending protrudes 5 cm. beyond the long burner. This is necessary for the gradual cooling of the gas stream to prevent possible dissociation of the carbon dioxide to carbon monoxide and oxygen which are not absorbed by the 50% potassium hydroxide solution.

Preparation for the Combustion. Stopcock *F* on top of the nitrometer is sparingly lubricated with the special stopcock grease; the barrel of the stopcock should become transparent, but no grease must enter the stem of the nitrometer, because deposits of grease at that point will not only cause the potassium hydroxide solution to froth but also lead to high results. The nitrometer is filled with 50% potassium hydroxide solution by opening stopcock *F*, raising the leveling bulb until the funnel is about one-fourth filled, then closing the stopcock and placing the leveling bulb in its lower ring clamp. The air is expelled from the combustion tube in the following manner: The gasometer is filled with carbon dioxide from the generating chamber of Kipp II by closing stopcock *D*, opening stopcock *C*, and lowering the mercury leveling bulb, by placing it on the table, until the mercury reaches the lower level in the gasometer; stopcock *C* is then closed, the leveling bulb placed in its open ring clamp, and stopcock *D* opened. Stopcock *E*, between combustion tube and nitrometer, is opened in such a way that the gases pass through the downward outlet into the air. About 100 ml. of carbon dioxide is passed through the combustion tube in this manner at a speed of about 50 ml. per minute, whereupon stopcocks *D* and *E* are closed, the gasometer refilled with carbon dioxide, and the washing-out repeated. After the second washing the long burner is lighted, centered under the combustion tube, and its flame so adjusted that it envelops the tube. The flame should be of sufficient intensity to heat the wire gauzes to a dark cherry red (650 to 700° C.), but excessive heating, because of its destructive effects upon the combustion tube, is to be avoided. Wire tunnels are placed over it, a long one, 19 to 20 cm., for the long burner, and a short one, 5 cm., for the movable burner, to reflect the heat downward. The gasometer is filled once more with carbon dioxide and about 80 ml. of it is passed into the air, after which stopcock *E* is turned cautiously to permit the gases to enter the nitrometer at a rate of two to three bubbles per second. A greater speed not only will result in poor absorption of the carbon dioxide by the potassium hydroxide solution, but also will break the fine film covering the mercury in the nitrometer, resulting in a subsequent sticking of the bubbles to the surface of the mercury. The bubbles rising from the inlet tube should be nearly absorbed by the 50% potassium hydroxide solution and show the char-

acteristics typical of microbubbles; they indicate the purity of the carbon dioxide as well as give assurance that the expulsion of the air from the combustion tube has been complete. Should the gas bubbles not be typical microbubbles the combustion tube is washed once more with about 80 ml. of carbon dioxide, which is passed into the air and the above test repeated. When microbubbles are obtained stopcock *D* is closed, stopcock *E* opened completely to the nitrometer, thus bringing the pressure in the combustion tube in equilibrium with atmospheric pressure. Then the leveling bulb is raised to the height of the funnel of the nitrometer, stopcock *F* opened, the collected gas bubbles forced into the funnel, stopcock *F* closed, and the leveling bulb placed in the lower ring clamp where it remains until the end of the combustion.

First Combustion. The combustion is started with a small flame of the movable gas burner 1 cm. in front of the copper oxide. The flame is gradually increased until it is about 5 cm. high and hisses slightly. As soon as the rapid evolution of gas bubbles, due to the application of additional heat, has subsided, the burner is slowly advanced toward the copper oxide filling, but its movement is controlled so that no more than one gas bubble per second, less rather than more, rises in the nitrometer. Disregard of this precaution leads either to low results, due to incomplete combustion of the substance or insufficient contact of the gases with the metallic copper to insure the reduction to elementary nitrogen of the oxides of nitrogen, which would be absorbed by the 50% potassium hydroxide solution; or to high results, which may be the consequence of the dissociation of the carbon dioxide to carbon monoxide and oxygen. Should the gas bubbles rise more rapidly, then the movable burner is removed until their frequency has returned to normal. The combustion is continued until the entire temporary filling up to the long burner has been thoroughly heated, which requires from twenty to twenty-five minutes. After the part of the combustion tube containing the substance has been passed with the burner, no more gas bubbles may rise and the receding of the mercury into the gas inlet tube of the nitrometer can be observed, indicating that the gaseous combustion products have passed their maximum expansion. The heating may then be speeded up somewhat, but nevertheless the heating must be continued until the permanent filling is reached. For some substances, especially those whose percentage of nitrogen is rather low, no nitrogen may be collected during the first combustion. In this event the time factor is the only guidance.

Second Combustion and Sweeping Out. With the first combustion completed, stopcock *E* is closed and the gasometer filled with carbon dioxide up to the beginning of the graduation. To bring the mercury

to the level of the first graduation mark, stopcock *D* is turned to connect the gasometer with the downward outlet, thus permitting the few milliliters of excess carbon dioxide to escape. Then stopcock *D* is turned to connect the gasometer with the combustion tube. It is of the utmost importance that stopcock *E* be opened very cautiously to the nitrometer, so that no more than three gas bubbles in two seconds pass into the nitrometer. Although a groove is etched into the bore of stopcock *E* to permit easier regulation, nevertheless it is advisable to practice the gradual opening of this stopcock before an analysis is started. To watch the mercury being forced back into the nitrometer may also be helpful, because it is not possible to see when the bore of the plug connects with the opening of the capillary tubing. With the speed so regulated that only three gas bubbles in two seconds rise in the nitrometer, the movable burner is placed once more in front of the temporary filling and the combustion repeated, only more rapidly, taking about ten minutes to heat the entire temporary filling up to the long burner. The movable burner is then extinguished, and, when the gas bubbles have become considerably smaller, their speed may be increased to two or three per second. When their size is again reduced to microbubbles, indicating that all the nitrogen has been washed out by the carbon dioxide, the rate of speed may be increased to five per second and the long burner extinguished. Fifty milliliters of carbon dioxide is usually sufficient for the sweeping out of the combustion gases, and when the mercury has reached the graduation mark in the gasometer indicating this volume, stopcock *D* is closed and stopcock *E* gradually opened completely until no more gas bubbles rise, thus again establishing the equilibrium with atmospheric conditions existing before the start of the combustion. Stopcock *E* is then closed and stopcock *D* opened again to permit the combustion tube to cool in an atmosphere of carbon dioxide. Failure to close stopcock *E* during the cooling of the combustion tube will cause the mercury in the nitrometer to be drawn into the combustion tube, thereby spoiling the filling and necessitating its replacement.

Determination of the Volume of Nitrogen. The leveling bulb is raised to the level of the 50% potassium hydroxide solution in the nitrometer by adjusting the upper ring clamp to the proper height. Gas bubbles remaining undissolved on the meniscus of the 50% potassium hydroxide solution in the nitrometer may be broken up by placing the leveling bulb in the lower ring clamp and striking the rubber tubing with the edge of the hand. After an interval of ten minutes, to permit the 50% potassium hydroxide solution to run down the inside wall of the nitrometer, the volume of nitrogen collected is read to the nearest 0.001 ml. with the aid of the magnifying lens. The barometric pressure is also read at this

time to within ± 1 mm. and the temperature of the 50% potassium hydroxide solution determined within $\pm 0.5^\circ$ C. by placing a thermometer in the funnel of the nitrometer and then in the leveling bulb. If the two readings do not coincide their average is taken.

Determination of the Air and Adsorption Error. Since the carbon dioxide supplied by the Kipp generator and the copper oxide used for the temporary filling always contain some residual air, which would cause high results, this air and absorption error must be determined and deducted from the total volume of nitrogen collected. The magnitude of this error, or, in other words, the amount of air contained in a given volume of carbon dioxide, 50 ml. in this case, is determined by combusting any substance which is free of nitrogen. However, it is not necessary to weigh this sample, although it should be approximately between 3 and 5 mg., but it is mixed with fine copper oxide as described and the combustion tube filled as for a regular determination. However, since not enough nitrogen will be collected from the residual air in 50 ml. of carbon dioxide to reach the calibration in the nitrometer which begins at 0.050 ml., some nitrogen is left in the stem from a previous determination, or air is let in by simply closing stopcock *F* when the 50% potassium hydroxide solution has reached a level between 0.150 and 0.200 ml. Ten minutes after the leveling bulb has been adjusted to the height of the meniscus the volume is read to the nearest 0.001 ml.; the temperature of the 50% potassium hydroxide solution and the barometric pressure are also taken at this time. The air is driven out of the combustion tube as described, except that for the testing of microbubbles not more than 1 ml. of carbon dioxide is used. The combustion and sweeping out of the gases with 50 ml. of carbon dioxide is carried out in exactly the same manner as in a regular determination. With the combustion completed, the leveling bulb is placed up to the meniscus of the 50% potassium hydroxide solution in the nitrometer, and ten minutes later the volume, temperature, and barometric pressure are determined. After the necessary corrections for possible temperature and pressure changes have been made, the difference between the reading before the combustion and after its completion represents the sum of the air and absorption error from the carbon dioxide and copper oxide. This error should be constant and vary no more than ± 0.002 ml. even over rather long periods of time; consequently, once this constancy has been established, it is not necessary to determine the air error every time the apparatus is used. An air and absorption error of 0.050 ml. for 50 ml. of carbon dioxide is tolerable, but a correctly set up apparatus will give an air and absorption error of 0.010 to 0.015 ml. for 50 ml. of carbon dioxide.

| Time: | Minutes |
|---|---------|
| Weighing of the sample..... | 10 |
| Filling and sweeping out the combustion tube..... | 15 |
| First combustion..... | 30 |
| Second combustion..... | 10 |
| Sweeping out of combustion products..... | 30 |
| Total..... | 95 |

Calculation:*Determination of the Net Volume of Nitrogen:*

Collected ml. of nitrogen (nitrometer reading),
 Minus, or plus, calibration correction (see nitrometer certificate),
 Minus air and adsorption error (determined by blank analysis),
 Minus 1.1% of total collected ml. of nitrogen (0.5% for adhesion of
 the 50% potassium hydroxide solution to the wall of the nitrometer,
 0.3% for the vapor pressure of the 50% potassium hydroxide solu-
 tion,* 0.3% for the temperature reduction of the barometric
 reading from room temperature to 0° C.)^{55, 56}

Instead of the above detailed corrections an overall correction of 2% may be deducted from the nitrometer reading already corrected for calibration errors.^{43, 44}

* This pressure correction may be subtracted directly from the barometer reading.³⁴

Percentage of Nitrogen:

Log of net volume of nitrogen,
 Plus log of 1 ml. nitrogen at temperature and pressure collected (see
 nitrogen reduction tables on pp. 301-310),
 Plus negative log of weight of substance;
 Antilog of total = percentage of nitrogen.

Remarks

The micro Dumas method as described here differs from the original procedure of F. Pregl^{43, 44, 47} mainly because of the introduction of a gasometer in the apparatus arrangement by J. B. Niederl and co-workers.^{38, 55, 56} The volume of carbon dioxide is measured and kept constant for every combustion, thereby eliminating the dependence upon the ill-defined microbubbles. C. Weygand⁵⁸ and others^{37, 38, 55, 56} have shown that the size of the microbubbles—all other experimental conditions remaining the same—depends upon the inside diameter of the gas inlet of the nitrometer and consequently may vary with different instruments. Furthermore, measurements with the gasometer show that the time required for the passing of a definite volume of carbon dioxide into the nitrometer while the same speed of the bubbles (one bubble per second) is maintained also depends largely upon the diameter of this gas inlet. It has been experimentally established that, whereas 30 ml. of carbon dioxide could be passed into one nitrometer in twenty minutes

by maintaining a rate of speed of one bubble per second, it required thirty minutes to pass the same amount of gas at the same rate of speed into another nitrometer having a narrower gas inlet. In the procedure described here the end of the combustion is given by the exhaustion of a definite volume of carbon dioxide in the gasometer; in the method of F. Pregl^{43, 44, 47} the end of the determination is given either by a time limit (thirty to forty minutes), also recommended by R. T. K. Cornwell,¹¹ or by the reappearance of microbubbles, which, according to F. Böck and K. Beaucourt,⁵ is an unreliable criterion. The empirical deduction of 2% from the volume of nitrogen as suggested by F. Pregl has been investigated by O. Trautz⁵⁵ and was found to consist of several factors, some of which are constant while others are subject to variation, as for instance the so-called air error, a circumstance which led to the adaptation of the calculation formula presented herein. A modified gasometer has been described by J. G. Sandza and J. F. Alicino.⁴⁹

A survey of the literature reveals that all phases and integral parts of the apparatus have been thoroughly investigated.^{17a} The open Kipp generator, as used by F. Pregl, has been largely discarded in favor of arrangements protecting the contents of the Kipp generator from contact with air.^{12, 24, 39, 51} A self-sealing carbon dioxide generator has been described by F. Hein²⁴ and E. J. Poth.⁴² The same purpose is accomplished by connecting two Kipp generators as described by S. Ogawa³⁹ and E. Diepolder,¹² which is particularly useful for double set-ups.²⁰ The arrangement described not only protects the contents of the Kipp generator delivering the carbon dioxide from contact with air but also permits convenient evacuation of the system and easy replacement of the expended acid with fresh acid whenever necessary without disturbing the air-tight connections of the apparatus. Thus such an arrangement needs to be dismantled only for the initial introduction of the marble, which is prepared according to the procedure of F. Pregl^{43, 44, 47} and A. Friedrich.¹⁷ Since the flushing out of the Kipp generator, as described by F. Pregl, is no longer necessary, such an apparatus will last for more than a thousand analyses.

Replacement of the Kipp generator as a source of supply of carbon dioxide by magnesium carbonate has been suggested by a number of investigators.^{13, 19} W. S. Ide²⁸ has demonstrated the successful application of the semi-micro magnesite method of E. Berl and H. Burkhart³ to milligram samples. This method, however, results in a much higher air error and also requires a complete new filling of the combustion tube for every determination. The use of fused sodium and potassium carbonate has been recommended by A. Meixner and F. Kröcker.³³ The use of sodium bicarbonate has been suggested by J. V. Dubskey¹³ and

others, but H. Fischer¹⁵ found that it does not offer any advantages over the preparation of carbon dioxide from marble. F. Breuer⁶ described an exchangeable carbon dioxide generator using sodium bicarbonate and the gasometer arrangement of J. B. Niederl and co-workers.^{38, 56} The use of solid carbon dioxide has been suggested for macro Dumas nitrogen determinations by F. Shea and C. E. Watts⁵² and for micro Dumas nitrogen determinations by E. B. Hershberg and G. W. Wellwood.²⁶ The last two have also devised for this purpose a suitable generator with adequate safety valve arrangements.

The apparatus (Fig. 24) consists of the dry-ice storage bottle (*a*), which is usually an ordinary commercial vacuum bottle of about 1-liter

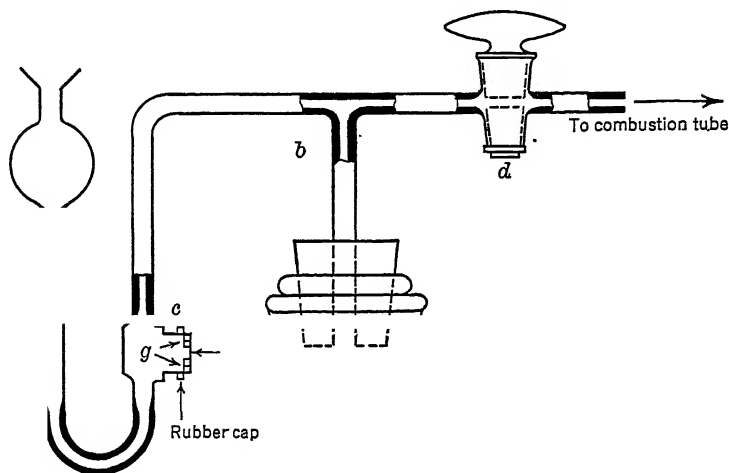


FIG. 24. Dry Ice Carbon Dioxide Generator.²⁶ Explanation in Text.

capacity, the thick-walled delivery tube (*b*), provided with a safety valve arrangement (*c*). The thick-walled vertical portion of the delivery tube (*b*) is 9 cm. long, its outer diameter is 9 mm., and its inner is 5 mm.; it extends through a tight-fitting rubber stopper into the dry-ice supply bottle (*a*). Its right horizontal side arm is 20 cm. long and of the same thickness and diameter; it carries a stopcock (*d*) and is connected to the combustion tube. The horizontal side arm at the left is of the same thickness and diameter. At a distance of 6 cm. from the vertical arm is the safety device. This consists of a vertical mercury U-tube manometer (*e*), which is 17 cm. long and is also of the same thickness and inner diameter. Eight centimeters below the horizontal arm the descending arm carries a paper diaphragm (*f*) for the release of the excess pressure.

The best pressure regulation is obtained by using as a membrane hardened filter paper of such porosity that the mercury cannot diffuse. It is advisable to insert a rubber washer (*g*) between the glass and the paper membrane to form a tight seal. When this is properly adjusted the fluctuation of the pressure is claimed to be less than 1 mm. After the supply bottle has been filled with dry ice, the apparatus is allowed to stand over night. The escaping carbon dioxide gas will sweep out all the air from the apparatus, and good microbubbles usually result the next day. A charge of about 1 pound of dry ice is claimed to last about 100 hours. For continuous operation the generator is recharged every fourth or fifth evening. Substitution of this type of generator for the Kipp generator arrangement has been found entirely satisfactory. Since the gasometer cannot be used in this type of generator, a time factor has to be introduced for the sweeping-out process and the empirical correction of F. Pregl^{43, 44, 47} of 2% surplus gas has to be applied in place of the detailed correction introduced by J. B. Niederl and co-workers.^{38, 56}

In regard to the combustion tube filling, with the exception of the suggestion to use iodine pentoxide instead of the metallic copper,⁴⁶ few changes have been reported and the original Pregl filling and arrangement have been found quite satisfactory,^{8, 9, 13, 16, 18, 21, 25, 31, 41, 54, 55, 57} as well as the combustion procedure and arrangement of the nitrometer.^{13, 32} A new nitrometer, featuring the elimination of the top stopcock, has been described by R. T. Milner and M. S. Sherman.³⁴

Occasionally substances are encountered which give low nitrogen values.^{17, 23, 34, 47, 48, 53} In dealing with them the addition of copper acetate to the sample has been suggested by D. F. Hayman and S. Adler.²³ Introduction of potassium chlorate into the combustion tube has been recommended by J. R. Spies and T. H. Harries.⁵³ The sticking of the gas bubbles to the surface of the mercury in the nitrometer was found to be due to such factors as too narrow an opening of the gas inlet of the nitrometer, too short a distance between this gas inlet and the level of the mercury, and excessive greasing of the stopcock connecting the combustion tube with the nitrometer. With the elimination or correction of these defects this difficulty is readily overcome; the suggestions of F. Pregl,^{43, 44, 47} O. Trautz,⁵⁵ B. Flaschenträger,¹⁶ and C. Weygand⁵⁸ that the surface of the mercury be dusted with powdered copper oxide have proved helpful. M. L. Nichols³⁶ recommends mercurous oxide for the same purpose.

Other innovations include: all-glass apparatus without any rubber connections whatsoever;^{35, 55} electric combustion furnaces;² simultaneous determination of nitrogen and carbon and hydrogen;⁴ replace-

ment of the nitrometer stopcock by a needle valve;²⁷ and placement of a screw adjustment on the elongated handle of this stopcock.

Since in the Dumas nitrogen method the reaction product is always determined volumetrically, the method without further modification, except for a slower combustion of the larger sample (8–15 mg.), lends itself most admirably for general use without a microanalytical balance,^{29, 30, 37, 38, 50} as recently demonstrated by J. B. Niederl and co-workers.³⁷ Earlier attempts involved solution or dilution methods.^{38, 50}

The development of semi-micro methods^{7, 10, 40} is usually governed by a similar desire, i.e., to eliminate microanalytical balances, and either comprises mere enlargement of the original Pregl micro Dumas apparatus, or combustions in vacuum^{7, 40} with either volumetric or manometric determination of the nitrogen.

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V. CARBON AND HYDROGEN DETERMINATION

Principle

A weighed amount of the organic compound is combusted in a measured volume of oxygen under controlled pressure to yield quantitatively carbon dioxide from the carbon and water from the hydrogen, the amount of these combustion products being determined gravimetrically. The combustion tube filling is so arranged that other elements present in the organic compound will not interfere with the final quantitative absorption of carbon dioxide and water by suitable absorption tubes containing appropriate absorbing agents.

$C + O_2 \rightarrow CO_2$ (absorbed by *Ascarite* [sodium hydroxide on asbestos])

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (absorbed by *Anhydron* [magnesium perchlorate])

Apparatus

The combustion train (Fig. 25) consists of the oxygen tank, the pressure regulator I, the drying tube II, the preheater III, the bubble counter and U-tube IV, the combustion tube V, the heating unit VI, the heating mortar VII, the water absorption tube VIII, the carbon dioxide absorption tube IX, the safety tube X, and the Mariotte flask XI.

Oxygen Tank. A standard commercial oxygen tank is used; it is provided with a pressure gauge and reduction valve to facilitate the control of the flow of oxygen.

Pressure Regulator (Fig. 25, I). The pressure regulator is connected to the oxygen tank by means of rubber tubing; it consists of two parts: the outer vessel or bottle, which is 21 to 22 cm. high and has a diameter of 4.5 to 5 cm., and the jacket with an inner tube 22 cm. long and 5 mm. in diameter. The bottle has a wooden head with two metal strips which hold the jacket in place, but nevertheless permit easy adjustment. The jacket has an inlet tube bent at right angles about 1 cm. above the point where it is sealed to the top of the jacket. This inlet tube extends the whole length of the jacket and about 5 mm. beyond its rim at the bottom. An outlet tube is sealed onto the jacket 1 cm. below its top

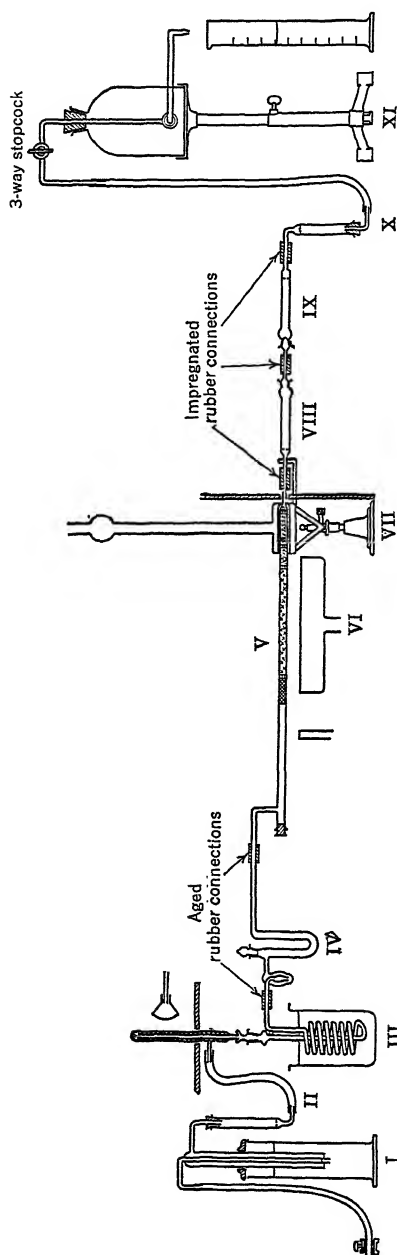


FIG. 25. I, Pressure Regulator; II, Drying Tube; III, Preheater; IV, Bubble Counter and U-Tube; V, Combustion Tube; VI, Heating Unit; VII, Heating Mortar; VIII, Water Absorption Tube; IX, Carbon Dioxide Absorption Tube; X, Safety Tube; XI, Mariotte Flask.

and extends horizontally about 4 cm. beyond it, where it is bent downward at right angles. This vertical arm of the outlet tube carries a drying tube filled with Anhydrone (Fig. 25, II). A rubber tubing 30 cm. long, which connects it to the preheater, is attached to the capillary outlet of the drying tube.

Preheater (Fig. 26). This device serves the purpose of combusting organic impurities present in the oxygen or given off by the rubber tubings through which it passes. It is about 30 cm. long over all and consists of a quartz combustion tube and a spiral of Pyrex glass which is connected to the combustion tube by a ground-glass joint. The diameter of the spiral tubing below the ground-glass joint is 5 mm. The combustion tube has a total length of about 16 cm. including the ground-glass joint and has a diameter of approximately 1 cm. The combustion tube proper is 10 cm. long and has an inner tube 9 cm. long and is 4 to 4.5 mm. in outside diameter. This inner tube is fused to the combustion tube about 6 cm. above the end of the ground-glass joint. An inlet tube of 4-cm. length and 6-mm. outside diameter is sealed to the combustion tube about 9 cm. from the top. The glass spiral is approximately 14 cm. long, and its coils have a spread of 3 to 4 cm. It ends in a vertical outlet tube which is bent horizontally at about the height of the ground-glass joint or 11 to 12 cm. from the bottom of the spiral. The horizontal arm of the outlet tube is about 8 cm. long and has an outside diameter of 5 to 5.5 mm., corresponding exactly to the outside diameter of the capillary tube of the bubble counter with which, when set up, it must form a glass-to-glass connection. The oxygen enters the preheater through the inlet tube, then passes through the heated copper oxide filling of the combustion tube into the inner tube and downward through the spiral which is immersed in a beaker containing water to cool the oxygen. The combustion tube is filled through the inlet tube with copper oxide in wire form about 2 mm. long and is heated by an electric heating cap or by a gas burner having a fishtail attachment for efficient heat distribution. As a rule, the copper oxide will last as long as the preheater itself, but when necessary it is removed by



FIG. 26. Preheater.

repeatedly tapping the combustion tube to loosen it and to enable it to fall through the inlet tube. Pieces of copper oxide which have become fused together and cannot be removed otherwise are dissolved by immersing the combustion tube in a solution of concentrated hydrochloric and nitric acid (1 : 1). Before being used again, or when new, the preheater is cleaned with cleaning solution, washed repeatedly with water, distilled water, rinsed with alcohol, and dried first on the suction pump and then in the drying oven at about 120° C.

Bubble Counter and U-Tube (Fig. 27). The purpose of the bubble counter is to provide a means of observing and checking the speed of the oxygen passing through the combustion train. The U-tube, of which the bubble counter is an integral part, is intended to absorb the carbon dioxide and water after the organic impurities present in the

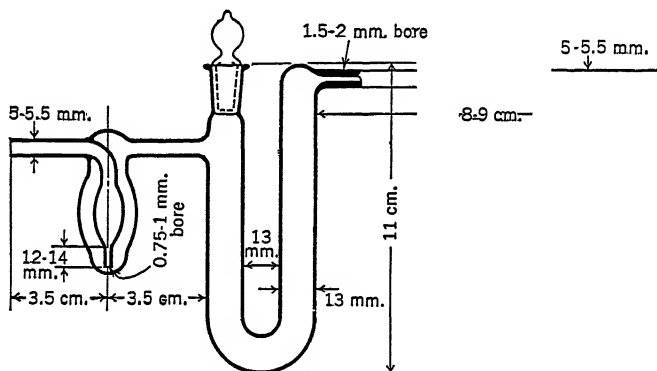


FIG. 27. Bubble Counter and U-Tube.

oxygen have been combusted by the preheater. An inlet tube of 3-cm. length and 5- to 5.5-mm. outside diameter is fused to the pear-shaped bubble counter, which is about 5 cm. long and 2 cm. in diameter. Inside the bubble counter the inlet tube is bent downward, expands to an outside diameter of 9 to 10 mm., and ends in a capillary 12 to 14 mm. long which has an aperture of 1-mm. maximum inside diameter; this capillary extends within 1 to 2 mm. of the bottom of the bubble counter. An outlet tube of about 2.5-cm. length and 5- to 6-mm. outer diameter, fused to the bubble counter opposite the inlet tube, forms a connection with the U-tube, to which it is sealed about 2 cm. below the rim of the ground-glass stopper. The U-tube is approximately 11 cm. long, and each arm has an outside diameter of 13 mm. It is provided with a capillary outlet tube of 8- to 9-cm. length, 5- to 5.5-mm. outside and

1.5- to 2-mm. inside diameter, or the same dimensions as the side arm of the combustion tube, with which, when attached, it forms a glass-to-glass connection.

After the bubble counter and U-tube has been cleaned with cleaning solution, washed with water and distilled water, and rinsed with alcohol, it is first dried under suction and then in a drying oven at about 120° C. The U-tube is filled as follows: A plug of clean, dry pliable glass wool is placed against the top of the sealed arm by means

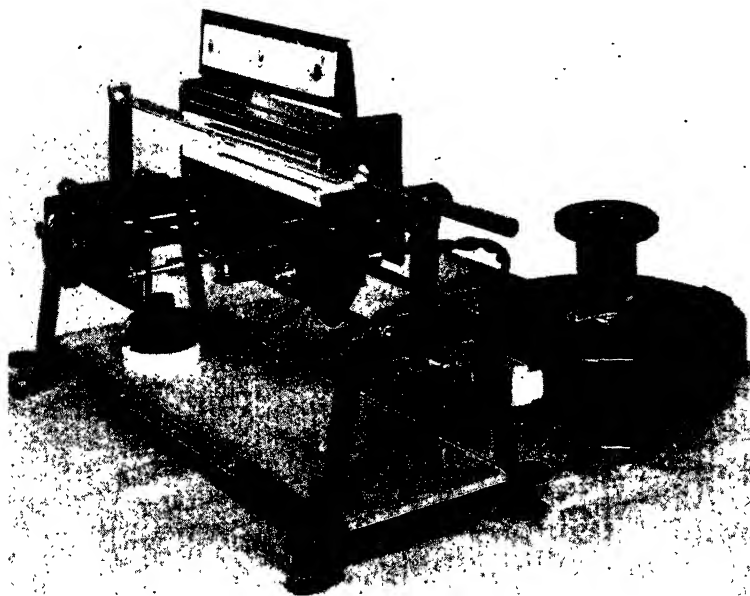


FIG. 28. Electric Combustion Furnace (American Platinum Works).

of a pliable wire, to prevent particles of Anhydrone from falling into the outlet tube. This arm of the U-tube is filled to its lower bend with Anhydrone which has been sifted through a sieve of 40 mesh to remove the powdery particles. Another plug of glass wool is pressed lightly against the Anhydrone, and the other arm of the U-tube is filled with Ascarite within 2 cm. of the inlet tube. A third plug of glass wool is placed against the Ascarite, and next to that a 2-cm. layer of coarse Anhydrone, intended to absorb most of the moisture present in the oxygen, which otherwise would soon clog up the Ascarite filling. The remainder of the U-tube is filled with pliable glass wool which prevents

shifting of the filling and precludes the possibility of Anhydrone falling into the horizontal tube connecting it with the bubble counter. To seal the U-tube the ground-glass stopper is warmed, covered with a little Krönig's glass cement and, while still warm, firmly fixed in place by turning it until the ground-glass joint has become transparent. Finally, enough concentrated sulfuric acid is introduced into the bubble counter with a pipet or capillary, and slight suction is applied from the outlet tube of the U-tube, so that the liquid extends 3 to 4 mm. above the capillary tip.

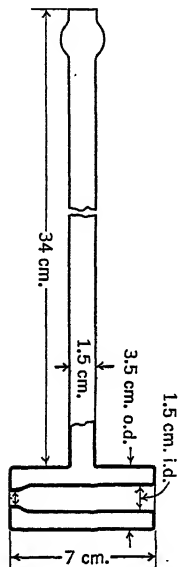


FIG. 29. Heating Mortar.

Heating Unit (Fig. 25, VI). Either a long gas burner or an electric heating unit may be employed, although the latter, for reasons of convenience and uniform heat distribution, is to be preferred. The long burner and combustion stand are of the same type as those for the Dumas apparatus (p. 84). For the movable burner a Tirrill or a Bunsen burner is preferable, because it has the advantage of permitting visual observation of the behavior of the substance during the combustion. The combustion tube is protected from the flames of the burners by pieces of wire gauze about 18 cm. long for the long burner and 5 cm. for the Tirrill or the Bunsen burner. If an electric heating unit is employed then the stand upon which the combustion tube rests is usually an integral part of the furnace and consequently may vary in shape or construction, but essentially it should be similar in its measurements to the stand shown in Fig. 21. A platinum-wired electric furnace shown in Fig. 28,^{3, 55} which

is movable in all directions, has been found very durable and efficient. Electric furnaces with automatic combustion arrangements are also known.^{48, 62, 84, 117}

Heating Mortar (Fig. 29). The latest type of heating mortar is a one-piece, all-glass apparatus. It is about 7 cm. long, 3.5 cm. in diameter, and has a reflux column 34 cm. high and 1.5 cm. in diameter with a bulb-shaped enlargement approximately 1 cm. from the top. The cylindrical chamber or jacket containing the constant-boiling liquid has a horizontal bore of 1.5-cm. diameter with a constriction at one end having an opening 6 to 8 mm. in diameter. This opening permits the passage of the capillary end of the combustion tube, but prevents the combustion tube itself from passing through. The cylindrical chamber rests on a curved metal plate and is fastened to the metal stand with

two adjustable metal bands. It is filled about two-thirds with *p*-cymene (b.p. 175–178° C.) and is heated by a microburner which is an integral part of the stand. A heavy copper wire approximately 6 cm. long and 3 mm. thick fits into an opening of the metal plate, where it is also heated by the microburner. This copper wire is placed over the capillary constriction of the water absorption tube during the combustion.

Combustion Tube (Fig. 30). The combustion tube may be of Supremax glass, Pyrex glass 172, or quartz; if of quartz it should be tested for leaks and if found defective must be rejected. It has a total length of 55 to 56 cm., an outside diameter of 10 to 11 mm., and an inside diameter of 8.25 mm. (± 0.25 mm.); it ends in a capillary 3 to 3.5 cm. long

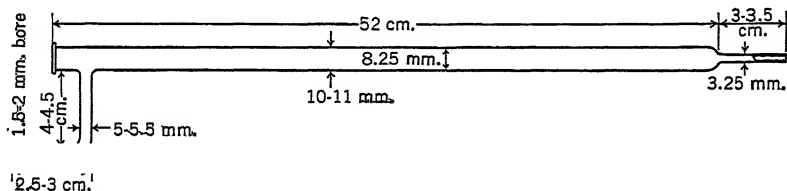


Fig. 30. Combustion Tube.

which has an outside diameter of 3.25 mm. (± 0.25 mm.) and a lumen of 1.5 to 2 mm. A right-angle side-arm inlet is fused on 1.5 cm. below its mouth; this side arm has an outside diameter of 5 to 5.5 mm. and an inside diameter of 1.5 to 2 mm. The arm which is sealed to the combustion tube is 4 to 4.5 cm. long, and the other, attached glass-to-glass with a 3-cm. length of aged rubber tubing to the outlet of the U-tube, measures 2.5 to 3 cm. in length.

COMBUSTION-TUBE FILLINGS

"Simple" Filling. This type of filling is for substances *not* containing nitrogen. It consists of a platinum wire gauze, silver wool, copper oxide, followed by another layer of silver wool. Since the lead peroxide, with its objectionable adsorption and absorption properties, is eliminated in this filling, excellent results, particularly hydrogen values, are obtained. No heating mortar is required.

"Simple Band" Filling. This filling is designed for compounds not containing nitrogen but possessing highly condensed ring systems (phenanthrene, chrysene, sterol type of compounds, etc.), particularly those containing an *angular* methyl group, which upon pyrolysis comes off in the form of methane, which often is likely to escape complete combustion by a mere copper oxide or copper oxide-lead chromate filling.^{106a, 113} The filling consists of five layers, each 3.5 cm. long.

Three layers, of copper oxide, are alternated with two layers of 30% platinized asbestos, as shown in Fig. 31. In addition, this filling has the usual layer of silver wool at the capillary end and a platinum wire gauze at the beginning of the filling. Also for this filling no heating mortar is required.

*"Combination" Filling.*⁹⁵ This type of combustion-tube filling is necessary for substances containing nitrogen. It is similar to the above *simple* combustion-tube filling, except that it contains a layer of lead peroxide after the oxidation filling which consists of the platinum wire gauze, copper oxide, and silver wool. The lead peroxide requires special heat treatment; therefore the heating mortar is necessary.

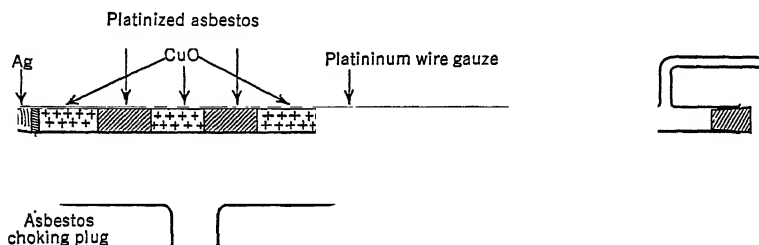


FIG. 31. Combustion Tube with the "Simple Band" Filling.

"Combination Band" Filling. This filling combines the features of the *simple band* filling with the *combination* combustion-tube filling. Thus it really becomes the filling of universal applicability, since any organic substance, those containing nitrogen as well as those giving low carbon values in insufficiently catalyzed fillings, can be analyzed satisfactorily. The filling consists of the alternating three layers of copper oxide and two layers of platinized asbestos, followed by silver wool and lead peroxide. A platinum wire gauze is placed at the beginning of the filling. The lead peroxide requires the inclusion of a heating mortar in the apparatus set-up.

Filling of the Combustion Tube. (Since the combustion train is needed to test the resistance of the combustion-tube filling to the pressure of oxygen while the tube is being filled, in order to avoid either insufficient or excessive pressure, the filling is done after all other parts of the apparatus are set up and connected.) After the combustion tube has been cleaned and dried as described on p. 83, the procedure of filling it with the *combination filling*, the one most widely used, is carried out as follows:

Silver wool or silver wire wound in spiral form is introduced into the combustion tube and placed against the capillary ending with a wooden

rod to form a loose layer 1 cm. long. This is followed by a 5- to 6-mm. compact layer of asbestos, the so-called choking plug. The purpose of this asbestos plug is to establish the correct resistance to the pressure of oxygen—an important factor, because excess resistance will slow down the flow of oxygen to below the required velocity; insufficient resistance, however, has the reverse effect. Ideal combustion conditions require a flow of 4 to 5 ml. of oxygen per minute through the system. The resistance offered by the choking plug is tested by attaching the combustion tube to the apparatus as shown in Fig. 25, but omitting the absorption tubes. To take into account the expansion of the asbestos upon heating, the liquid in the heating mortar is brought to boiling.

After the safety tube has been attached to the combustion tube, the side arm of the Mariotte flask is lowered to a horizontal position, the pressure regulator adjusted to 3 cm. below the level of the liquid, and the amount of water displaced in the Mariotte flask by the oxygen measured with a graduate cylinder. The choking plug has the correct resistance if 7 to 8 ml. of oxygen passes through the system per minute under the above conditions. If insufficient or excessive pressure is observed, it must be remedied by either adding more asbestos or removing part of the choking plug already in the combustion tube. When the correct resistance has been attained the combustion tube is removed from the apparatus and its inside wiped with a cotton wad wound around a stiff iron wire to remove asbestos fibers adhering to the side wall. Next, a 3.5- to 4-cm. layer of lead peroxide is added and the combustion tube gently tapped to avoid the formation of air pockets between the granules of the reagent. The combustion tube is again wiped with a cotton wad to remove the powder of lead peroxide from its side walls. This cleaning is repeated three or four times, and then another asbestos plug 1 to 2 mm. long is gently pressed against the lead peroxide to hold it in place. The combustion tube is again attached to the apparatus and its resistance tested; a flow of 5 to 6 ml. of oxygen per minute through the system under the conditions stated above should be obtained. The combustion tube is wiped clean of asbestos fibers, and enough silver wool or spirals of silver wire are added to form a layer 3.5 to 5 cm. long which, depending upon the measurements of the set-up, are distributed as follows: 1 to 2 cm. are to be within the heating mortar; 0.5 to 1 cm. to cover the space between the mortar and the electric furnace or long burner; and 1 cm. to extend into the heating unit. An asbestos plug 1 to 2 mm. long is placed against the silver wool and then copper oxide is added. The exact length of this filling depends on the measurements of the electric furnace or long burner, but enough oxidizing agent is added, a small portion at a time and with repeated tapping,

to form a compact layer approximately 14 cm. long, but still 2 to 2.5 cm. from the end of the heating unit. The combustion tube is again wiped clean and another asbestos plug 1 to 2 mm. long is lightly pressed against the copper oxide. A platinum wire gauze of 60 to 80 mesh and measuring 3 by 5 cm., rolled around some silver wire to form a cylinder 7 mm. in diameter and 3 cm. long, is pushed into the combustion tube with a glass rod; the platinum gauze should extend about 1 cm. beyond the heating unit. (The correct distribution of the filling of the combustion tube is shown in Fig. 32.) Finally, the combustion tube is again attached to the apparatus and its resistance to the flow of oxygen is tested once more. The additional filling should have reduced the flow of oxygen to 3 to 4 ml. a minute. To obtain additional pressure the jacket of the pressure regulator is depressed to give a head of 4 to 5 cm. During

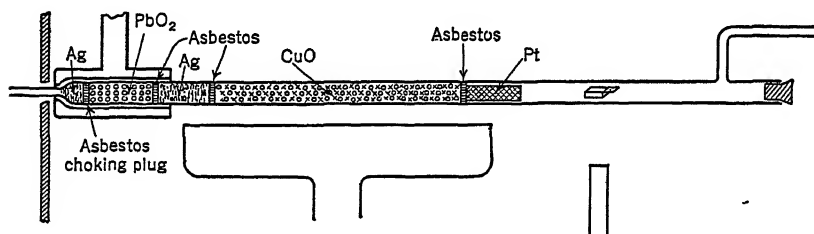


FIG. 32. Combustion Tube with the "Combination" Filling.

these tests, which are made to establish the correct pressure in the system, the side arm of the Mariotte flask should remain in a horizontal position; changes in the pressure should be made by the pressure regulator, and the side arm of the Mariotte flask is to be used only for the final or exact regulation, so that it is never more than a few degrees off its horizontal level.

Conditioning of the Combustion Tube. A freshly filled combustion tube must be heated for a period of time before it can be used for analyses. This preheating is carried out by attaching the combustion tube to the apparatus, but leaving its capillary end open and adjusting the pressure regulator to a delivery of 3 to 4 ml. of oxygen per minute. The combustion tube is heated for at least 8 hours, or preferably over night, with all the heating units showing the normal combustion temperature of 700°C . ($\pm 25^{\circ}\text{C}$). This preheating process, however, causes an abnormal dehydration of the lead peroxide and consequently the first few analyses usually give a low hydrogen content. To restore the moisture equilibrium, the combustion of a few unweighed samples (approximately 10 mg.) is advised.

When not in use, the combustion tube is closed by attaching the safety tube of the Mariotte flask to its capillary end; it is always kept under pressure of oxygen to prevent atmospheric vapors from entering the system. A combustion tube protected in this manner will remain in good condition even after prolonged idleness and need only be heated for several hours before a combustion is carried out.

In the *simple* combustion-tube filling the filling operation and the tests for the gas-flow resistance remain the same, except that the lead peroxide is omitted. No heating mortar is required; however, the capillary outlet of the combustion tube must be adequately insulated against overheating.

A similar procedure is followed for the *simple band* filling. Also here the lead peroxide and heating mortar are omitted. Instead of a single layer of copper oxide, however, three layers of copper oxide, each separated from the other by a layer of 30% platinized asbestos, as shown in Fig. 31, are used; each layer is 3.5 cm. long. Although the platinized asbestos layers should be fairly compact, they must not be pressed together too tightly, for otherwise excessive resistance to the flow of oxygen would result. Thus it is advisable to test the flow of oxygen through the system after the introduction of each layer of platinized asbestos and make certain that the pressure obtained fulfills the requirements stated in the paragraphs describing the filling of the combustion tube (p. 108).

The *combination band* filling is identical with the *combination* filling, i.e., retention of the lead peroxide and the heating mortar, but with replacement of the single copper oxide layer by alternate 3.5-cm. layers of copper oxide and platinized asbestos, as described for the *simple band* combustion-tube filling.

The combustion tube always should be adequately protected from the flames of the long burner by a fine-mesh wire gauze which is somewhat longer than the burner, and from the flame of the Tirrill or the Bunsen burner by a wire gauze about 5 cm. long. If an electric furnace is employed the long wire gauze is omitted; no wire gauzes are needed for a quartz combustion tube.

Absorption Tubes (Fig. 33). Because the accuracy of a carbon and hydrogen determination depends considerably upon the constant weight attainable by the absorption tubes, their construction and also their measurements, especially those of the capillary constrictions, are of utmost importance. The water absorption tube is approximately 17 cm. long over all. The filling chamber has a diameter of 8 to 9 mm. and is 8 to 9 cm. long; it is separated from the adjoining air chamber by a thin glass wall having an aperture of 0.20 to 0.25 mm. The absorption

tube ends in a capillary tubing of about 3-cm. length and 3.3- to 3.5-mm. outside diameter, or the same diameter as specified for the capillary ending of the combustion tube. This capillary tubing of the absorption tube has two constrictions, each being 5 mm. long and having an inner diameter of 0.20 to 0.25 mm.; the two constrictions are separated from each other by an air chamber 3 mm. long and 2 to 2.5 mm. in inner diameter. This design of the capillary ends is intended to reduce the diffusion with atmospheric vapors, especially moisture, thus contributing greatly to the constancy of weight attainable by the absorption tube. The so-called head or open part of the absorption tube has a ground-glass joint provided with a hollow ground-glass stopper which has an aperture 0.2 to 0.25 mm. in diameter at its curved base; its opposite

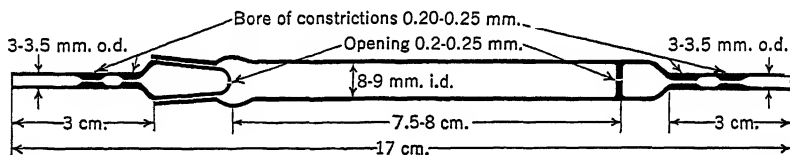


Fig. 33. Absorption Tube.

end is drawn out to a capillary tubing of the same construction and measurements as the end of the absorption tube.

The carbon dioxide absorption tube is identical in construction and measurements with the water absorption tube.

Water Absorption Tube. The water absorption tube is cleaned by washing with distilled water and rinsing with alcohol afterwards. It is dried by being placed first on the suction pump, next in a drying oven kept at 120° C. This is followed by another drying on the suction pump to remove the alcohol vapors completely. The tube is filled by placing a 3- to 4-mm. layer of pliable glass wool against the end of the filling chamber, which is intended to protect the aperture of the glass wall from particles of Anhydrone. A 1.5- to 2-cm. layer of coarse Anhydrone (flakes 3 to 5 mm. long) is then introduced, followed by another 3- to 4-mm. layer of loosely packed glass wool. The rest of the absorption tube, to within 5 mm. of the ground-glass joint, is filled with fine but not powdered Anhydrone. Another wad of glass wool, filling the remaining space in the absorption tube, completes the filling. The ground-glass stopper is warmed outside the flame of a microburner and a little Krönig's glass cement is applied to the warm surface of the stopper, which is then quickly inserted and rotated in the ground-glass joint of the absorption tube; a transparent seal should be obtained. If insufficient cement has been applied, the ground-glass joint is warmed outside

the flame with constant turning until the cement softens and the stopper can be removed. More cement is then applied and the sealing repeated. Excess cement must also be avoided, lest the aperture at the base of the stopper should become clogged when the stopper is placed in the ground-glass joint. The excess cement collecting on the rim of the ground-glass joint is removed with a cotton tuft dipped in benzene.

Carbon Dioxide Absorption Tube. After the tube has been cleaned as described above, a wad of pliable glass wool, followed by a 2.5- to 3-cm. layer of fine Anhydrone, is introduced. Another small wad of glass wool is then introduced and the rest of the tube is filled with Ascarite within 5 mm. of the ground-glass joint. A third layer of glass wool is added and the absorption tube sealed as described above.

Before the absorption tubes are used for an analysis, their resistance to the flow of oxygen or air must be tested. They are attached to each other head-to-head with a thick-walled rubber tubing 3 cm. long. Another such rubber tubing is placed on the free end of the water absorption tube, and the absorption tubes thus connected are attached to the capillary ending of the Ascarite-Anhydrone tube of the aspirator; the free end of the carbon dioxide absorption tube is connected to the safety tube of the Mariotte flask. Then the side arm of the Mariotte flask is adjusted to a horizontal position, and under this condition a minimum flow of 3 ml. of air per minute should be obtained. Fifty milliliters of air is drawn through the system in this manner and then, if the filling permits the passage of air at the above-mentioned velocity, the tubes are ready for use; otherwise it must be determined which one of the tubes is filled too tightly by attaching them separately. The faulty absorption tube must be refilled because a greater resistance than stated above may lead to difficulties soon after a few analyses, owing to the increase of the resistance as the filling of the absorption tubes is gradually used up.

Counterpoising the Absorption Tubes. According to F. Pregl^{106b} the absorption tubes may be counterpoised with open tare bottles containing lead shot, and to distinguish them from each other they are provided with numbers or letters, for example, *H* for the Anhydrone tube and *C* for the Ascarite tube. This form of counterpoising has been found entirely satisfactory when running analyses on days with slight temperature and humidity changes. Since lead shot tends to take up moisture—10 grams takes up as much as 6 micrograms per 1% increase in humidity,¹²⁸ a tare bottle with a ground-glass stopper should be employed. Glass beads may be substituted for the lead shot, but then much larger tare bottles are required. Another method of counterpoising the absorption tubes involves the use of a so-called tare absorp-

tion tube.^{52, 93} Three absorption tubes of approximately equal weight are selected. One serves as the water absorption tube and the second as the carbon dioxide absorption tube. Both are filled according to the directions given above but, for the time being, are not sealed. The third absorption tube serves as the tare for the two others and is filled half with Ascarite and half with Anhydrone. The weight of the three tubes is adjusted while they are still open by inserting or removing appropriate amounts of absorption reagents until their weights are within 0.5 gram of each other. Then they are sealed as usual. The tare absorption tube undergoes identical wiping and weighing treatment and is attached to the other two during the combustion in such a manner that the Ascarite layer is adjacent to the carbon dioxide tube and the layer of Anhydrone faces the safety tube of the Mariotte flask. In the actual weighing of the absorption tubes, the tare absorption tube is placed on the hooks of the right-hand pan of the balance. Thus not only does the tare absorption tube serve as a control^{41f} but also, since it undergoes identical treatment with the absorption tubes, any climatic influences such as changes in temperature, atmospheric pressure, and humidity are automatically taken care of.

To prevent the absorption of water or carbon dioxide by the absorption tubes when they are not in use, so-called *protection caps*—thick-walled rubber tubing stoppered at one end with a fire-polished glass rod, or rubber stoppers having a bore that extends to only half the length of the stopper—are placed over the capillary constrictions.

Drying Tube and Safety Tube (Fig. 25, II, X). The purpose of these tubes is to absorb moisture that may emanate from the pressure regulator or the Mariotte flask. The tubes are identical in size and construction and are 13 cm. long and 10 to 12 mm. in diameter. Each tube is open at one end and has an air chamber at the other which terminates in a capillary bent at a right angle which is 3 to 3.5 cm. long and has an outer diameter of 4 mm. The tube is filled with Anhydrone, and a fairly tight layer of pliable glass wool is placed before and after the filling. The open end is closed with a rubber stopper through which a capillary bent at a right angle is inserted. A rubber tubing about 30 cm. long connects the drying tube to the preheater and another of approximately 60-cm. length connects the safety tube to the Mariotte flask.

Mariotte Flask (Fig. 25, XI). The purpose of the Mariotte flask is to measure the volume of the oxygen passing through the system and, is to measure the volume of the oxygen used in the combustion and, furthermore, to supply sufficient suction to overcome the resistance

offered by the absorption tubes, so that approximately atmospheric pressure prevails at the rubber connections between the capillary end of the combustion tube and the water absorption tube and between the latter and the carbon dioxide absorption tube. Maintenance of atmospheric pressure conditions at these points is quite important in order to minimize either loss of combustion gases in case of excess pressure, or assimilation of moisture from the air in case of reduced pressure. The Mariotte flask may be of 1- or 2-liter capacity, the larger size being preferable because it permits the carrying out of at least eight determinations without refilling. A glass tube or side arm is fixed into the lower tubulure of the flask by means of a perforated cork stopper, an arrangement which permits easy adjustment of the side arm. The side arm should have a length equal to the height of the Mariotte flask



FIG. 34. Aspirator.

(23 to 25 cm. for a 2-liter flask); it has an outside diameter of about 5 mm. and a bore of 3 mm. It is bent at a right angle about 5 cm. from the end which is inserted into the cork. The other end is bent vertical to the horizontal side arm and drawn out to a capillary tip of 1- to 1.5-mm. bore and 2.5- to 3-cm. length. The neck of the Mariotte flask is provided with a one-hole rubber stopper; a glass tube of about 3-mm. bore, bent twice at a right angle and carrying a three-way stopcock⁶⁸ between the bends, is inserted through the rubber stopper and extends almost to the bottom of the flask. The Mariotte flask is placed high enough on a suitable stand so that a 250-ml. graduate cylinder, in which the actual displacement of water by the oxygen during the combustion is measured, can conveniently be placed under the horizontal side arm.

*Aspirator*⁹⁷ (Fig. 34). To replace the oxygen in the absorption tubes with air after the combustion and to cool them quickly to the temperature of the balance room, which is necessary, a separate unit, *the aspirator*,

is employed. It is completely separated from the combustion train and, because of its simplicity and mobility, can be quickly set up in any convenient place in the balance room or near the balance, a circumstance which greatly aids in obtaining the much-desired constancy of weight of the absorption tubes. This aspirator consists of a wash bottle of 250-ml. capacity, a combustion tube—which may be an old, though clean, combustion tube—a drying tube, and a 1-liter Mariotte flask. The wash bottle contains about 70 ml. of concentrated sulfuric acid. A combustion tube, cut to a length of 25 cm., but with the capillary end in perfect condition, and its mouth provided with a perforated, tight-fitting rubber stopper into which a capillary glass tubing is inserted, is connected with a good rubber tubing to the exhaust of the wash bottle. The filling of the aspirator tube consists of the following: a plug of pliable glass wool approximately 5 mm. long is placed against the capillary ending; then a 10-cm. layer of Anhydrone is introduced, followed by a wad of glass wool and a 10-cm. layer of Ascarite; a third plug of glass wool is placed against the Ascarite and the rest of the tube is filled with Anhydrone, which is followed by another layer of glass wool. This filling is designed to remove carbon dioxide and moisture from the air which is passed through the absorption tubes after the combustion. The Mariotte flask, placed on a stand as illustrated, has the same side-arm arrangement and stopcock tubing at the top as the one of the combustion train. Rubber tubing about 50 cm. long leads from the top of the Mariotte flask to the safety tube, which is filled with Anhydrone. The right-angle capillary tube of this safety tube carries a thick-walled rubber connection about 3 cm. long with which it is attached to the carbon dioxide absorption tube when in use, or to the capillary ending of the aspirator tube when not in use. A silk thread is attached to the delivery tube of the Mariotte flask to test for electric charges on the absorption tubes after they have been wiped.

MISCELLANEOUS

Flannel. A piece of flannel about 10 cm. square is kept in a Petri dish. It is moistened before use, but should not be wet; excess moisture must be removed by squeezing the flannel and pressing it between the folds of a towel.

Chamois. Several pieces of chamois about 10 cm. square are needed and are kept in a Petri dish. They should be of a good grade of soft leather and should be freed of fat and other impurities when new, and whenever necessary thereafter, by washing them thoroughly with soap and warm water to which a little ammonium hydroxide has been added.

They are rinsed thoroughly and dried at room temperature. To prevent the accumulation of electric charges on the absorption tubes when wiping them on very cold or dry days, it is recommended that a slightly moist flannel be placed on the bottom of the dish in which the chamois are kept.

Rubber Tubing. The rubber tubing from the oxygen tank to the pressure regulator and thence to the preheater should be of a good grade and about 7 mm. in outside and 4.5 to 5 mm. in inside diameter. It is not necessary to subject it to the aging process if a preheater is employed in the combustion train, although impurities present in the bore such as powder or talcum should be removed.

Rubber Connections. The rubber connections between the preheater and the bubble counter and between the U-tube and the side-arm inlet of the combustion tube must be of seamless and aged rubber tubing of 3.5-, to 4-mm. bore and the thickness of the wall should be at least 1 mm. The rubber connections employed for the absorption tubes are of thick-walled, seamless impregnated rubber tubing of about 1-cm. outside diameter and 2-mm. bore (± 0.25 mm.). The process of impregnation is carried out by cutting vacuum rubber tubing of the above dimensions into pieces 3 cm. long, placing them in a 500-ml. round-bottomed flask containing 150 to 200 ml. of pure vaseline or paraffin wax, and heating them on the water bath for about twenty minutes. While still warm the flask is then evacuated on the suction pump, and as soon as the contents have ceased to foam the vacuum is broken to admit the air which forces the paraffin or vaseline into the pores of the rubber tubing. This procedure of boiling and evacuation is repeated several times until at a reduced pressure of 10 to 15 mm. no further rising of bubbles is observed. The paraffin or vaseline is permitted to drain off while still warm and the rubber tubings are wiped clean on the outside with a clean cloth and the bore with tufts of cotton moistened with a little benzene and finally with dry cotton. The impregnated and cleaned rubber tubings are stored in a desiccator over Anhydrone.

The two rubber connections for the absorption tubes are marked I and II, so that their respective positions are always maintained. Rubber connection I is placed at the end of the water absorption tube and II between the water absorption tube and the carbon dioxide absorption tube. In addition, an arrow may be painted on the rubber connections to indicate the direction of the gases passing through them; this assures identical placement each time they are attached. Correct placement is especially important for rubber connection I, one end of which becomes prematurely decomposed by its exposure to the warm capillary end of the combustion tube.

Stopper for the Combustion Tube. Although not free of objectionable properties, such as porosity and hygroscopicity, a smooth, tight-fitting cork is best suited for this purpose. Rubber stoppers meet with disfavor because particles of rubber break off after short usage and may be carried to the area of the combustion when the platinum boat or foil is introduced.

Assembling the Combustion Train

A table of convenient height and suitable length (1 meter high and 2 meters long) which allows easy access to, and complete survey of, all parts of the apparatus, should be chosen as the basis of the set-up. Depending upon its size and the space available, the oxygen tank is placed close enough to the combustion train so that a 30- to 40-cm. length of rubber tubing, attached to the outlet of the reduction valve, is sufficient to connect it to the pressure regulator.

(With the exception of the combustion tube, for the filling of which a completed set-up is required, all other parts of the apparatus should be ready for attachment. Such glass parts as the pressure regulator, drying and safety tubes, preheater, bubble counter, and U-tube are cleaned, dried, and filled as previously described.)

The pressure regulator, following the oxygen tank in the order of the set-up, is filled to two-thirds of its capacity with dilute sulfuric acid (1:1). The vertical end of the intake tube of the pressure regulator is moistened with a trace of glycerin, and then the rubber tubing leading from the oxygen tank is placed over it. The rubber tubing should have a bore of 3.5 to 4 mm., or an inside diameter smaller by 0.5 to 1 mm. than the outside diameter of the glass tube, to insure a gas-tight connection. Rubber tubing having a bore considerably smaller than stated is unsuitable, because as the result of excessive stretching it soon develops cracks at the joints and, consequently, leaks. The outlet tube of the pressure regulator is moistened with a trace of glycerin and inserted in the perforated rubber stopper of the drying tube. A rubber tubing approximately 25 cm. long is attached to the right-angle capillary tube of the drying tube and connected to the inlet of the preheater. To insure tight connections and a leak-proof system all rubber tubings should be placed 1.5 to 2 cm. beyond the end of the glass tubing to which they are attached.

The preheater is fastened to a suitable metal stand in the following manner: A cylindrical cork, cut open parallel to its axis and having a bore of 6 to 7 mm., is placed just below the combustion tube of the preheater which is attached to the stand with a suitable clamp. The spiral, fastened to the preheater with two wire springs, is immersed in a

conical beaker three-fourths filled with water and held at the proper height by a ring clamp. Another ring clamp, placed over the combustion tube at about the height of the inlet tube, serves as a support for an asbestos shield or Transite plate approximately 15 by 15 cm. with an opening in the center so that it can be placed over the vertical combustion tube. This shield protects the rubber tubings at both ends from the effects of the heat from the electric heating unit or the gas burner. If a Tirrill or Bunsen burner is used, it is provided with a wing top to effect an efficient heat distribution over a larger part of the combustion tube. The height of the preheater is so adjusted that its outlet tube is on the same level as the inlet tube of the bubble counter.

The bubble counter and U-tube is either suspended from a stand with a wire stirrup or loosely held in place or supported by a clamp attached to a small stand. It is held at such a height that the outlet tube is level with the side arm of the combustion tube. The inlet tube of the bubble counter is connected glass-to-glass to the preheater and the U-tube glass-to-glass to the side arm of the combustion tube, as shown in Fig. 25. The rubber tubings with which these connections are made must be of best-quality impregnated material and are about 3 cm. long, of 6-mm. external and 4-mm. internal diameter. They should be moistened as little as possible when they are attached, and they have to be pushed over the glass tubings as a tight-fitting glove is drawn over the fingers. When the bubble counter or the combustion tube is removed it is better to cut off these rubber connections, because after some time they will adhere to the surface of the glass. Other means of removal than cutting will incur considerable risk of breakage. By attaching the bubble counter and U-tube to the apparatus glass-to-glass, the possibility of organic matter being taken up by the oxygen at these points is practically eliminated. And since combustible impurities present in the oxygen either originally or because of the contact of the oxygen with the two longer rubber tubings before and after the pressure regulator, are combusted by the preheater to carbon dioxide and water and subsequently absorbed by the filling of the U-tube, these rubber tubings, otherwise a potential source of trouble, should no longer be the cause of high carbon and hydrogen values.

The long gas burner, the combustion stand, and the heating mortar are assembled next. The height of the heating mortar is adjusted so that the combustion tube fits into the central passage but still rests on the V-shaped notches of the stand. A strip of asbestos paper, 6 cm. long and 1.5 cm. wide, is placed in this passage under the combustion tube to give it some support without, however, obscuring the combustion tube, visible through the glass heating mortar. A disk of heavy

asbestos paper, or several to bring it to 2- to 3-mm. thickness, is cut to conform to the diameter of the glass jacket to fit between the heating mortar and the combustion stand. The other end of the heating mortar which faces the absorption tubes is similarly provided with a disk of asbestos paper and then with an asbestos shield or Transite plate about 30 cm. high and 20 cm. wide, having an opening at the proper height to permit the passage of the capillary ending of the combustion tube. This shield is necessary to protect the absorption tubes from the heat emanating from the heating unit. It should be tied to the heating mortar with a pliable wire to keep it firmly in place. The long gas burner is placed under the stand and 1.5 cm. away from the heating mortar. Its height is so adjusted that the wire gauze of the combustion tube is covered by its flames, which should be of sufficient intensity to heat the wire gauze to a dull red.

If an electric furnace is employed^{3, 55, 84, 117} its temperature must be adjusted to 700° C. ($\pm 25^\circ$) by means of a suitable resistance; furthermore, it is necessary to test the heating element of the furnace at both ends as well as in the middle with a pyrometer for its uniformity in temperature ($\pm 25^\circ$ C.). A furnace which shows greater variations in temperature is unsuited for service. The electric furnace and the heating mortar are joined to each other as closely as possible. For the sake of greater stability it is advisable to fasten the one to the other with flexible wire.

With the Mariotte flask assembled and placed after the combustion train proper, as shown in the illustration, and the combustion tube filled and attached, the set-up of the carbon and hydrogen apparatus is essentially completed. The next step is to test the system for possible leaks, because it is quite obvious that leakages in the combustion train must be eliminated, first in order to avoid loss of combustion gases and second because only a gas-tight system will give the correct pressure conditions so essential for a satisfactory determination. The principal sources of leaks are the various rubber connections and are due either to poor-grade, very porous rubber tubings, or to tubings of improper diameter, for if the diameter is too large, the connection will not be tight enough to withstand the pressure within the system, and if too narrow, the tubing will be unduly stretched, resulting in excessive porosity. However, it is also possible that some glass part of the apparatus may have a small crack which might be responsible for the leak and, therefore, a thorough inspection of the entire system is necessary.

The apparatus is tested for leaks as follows: First, the pressure regulator is depressed to give a head of about 5 cm. and the capillary end of the combustion tube is closed with a thick-walled, tight-fitting rubber

connection stoppered with a glass rod. Then the oxygen is turned on and the flow so regulated that about one bubble per second overflows from the jacket in the pressure regulator. If the level of sealing liquid inside the jacket remains the same and if at the same time no bubbles rise in the bubble counter, the apparatus can be considered air-tight and free of leaks. If, however, the meniscus of the sealing liquid in the jacket of the pressure regulator rises and if at the same time bubbles appear in the bubble counter, there might be not only one but several leaks. Rising of bubbles in the bubble counter always indicates a leak in the combustion train. Rise of the meniscus of the sealing liquid in the jacket of the pressure regulator, with absence of bubbles in the bubble counter, indicates a leak in the purification train between the pressure regulator and the bubble counter. The leaks may be detected by applying a little water to the connections under suspicion. In the event of a large leak, the faulty rubber connection must be replaced by a better one; if it is only a slow leak, that is, if only one bubble in ten or fifteen seconds passes into the jacket of the pressure regulator, these connections may be made leak-proof by painting them with a little shellac or collodion. During this operation and while the material is allowed to dry, it is necessary, of course, to reduce the pressure in the system to approximately atmospheric. After the painted connections have dried and all leaks have been eliminated, the apparatus, with the combustion tube attached, is heated for a period of at least eight hours or preferably over night. The exposed part of the combustion tube is also heated with a Tirrill or Bunsen burner for about thirty minutes, beginning from a safe distance from the cork stopper (about 5 cm.) up to the long burner or electric furnace. Finally, a blank analysis is carried out as described on p. 126, and if the increase in the weight of the absorption tubes is within tolerable limits—0.04 mg. for the water absorption tube and 0.02 mg. for the carbon dioxide absorption tube—then the apparatus is ready for use.

Reagents

Anhydrone (Magnesium Perchlorate).⁷ It is sifted to remove the powder and separated into coarse and fine particles, the former representing flakes several millimeters long, and the latter being 1 mm. square or less. The two sizes are saturated with carbon dioxide and stored separately in wide-mouth ground-glass stoppered reagent bottles.

Ascarite (Sodium Hydroxide on Asbestos).¹³¹ This commercial reagent can be used without further preparation; in filling the carbon dioxide absorption tube, however, larger pieces of asbestos should be

avoided. It is stored in a wide-mouth ground-glass stoppered reagent bottle.

Asbestos. Gooch crucible asbestos is used for the asbestos plugs in the combustion tube. It is ignited in a porcelain crucible to red heat in an electric furnace for thirty minutes and is stored in a wide-mouth ground-glass stoppered reagent bottle. If an electric furnace is not available, the asbestos may also be ignited just before being used by holding small amounts with the platinum-tipped forceps in the slightly hissing, non-luminous flame of a gas burner.

Copper Oxide (Cupric Oxide).^{7, 120} Copper oxide is crushed to pieces of 3- to 4-mm. length; particles smaller than 20 mesh are sifted out. The accepted portion is ignited in a porcelain crucible in an electric furnace at 800 to 900° C. for about thirty minutes with occasional stirring. If an electric furnace is not available, the crucible is placed in a larger one which rests on the heavy asbestos shield provided with an opening large enough so that the larger crucible can be heated effectively with a hot flame. The copper oxide is ignited with a strong flame for about one hour with occasional stirring.

Pliable Glass Wool (Corning Brand Fibre Glass No. 008).

Lead Peroxide (Lead Dioxide, Lead Superoxide, PbO_2).^{106a, 113} Because only high-grade lead peroxide will give satisfactory results, it is necessary to devote considerable care to the preparation of this reagent or, if obtained from a commercial source, to test its purity. Commercial lead peroxide is purified and prepared as follows: About 100 grams of lead peroxide is digested with concentrated nitric acid in an evaporating dish on the steam bath for about two hours with occasional stirring. After standing for one hour the nitric acid is decanted and the product is washed with distilled water until the test of the wash water with diphenylamine-sulfuric acid is negative. The material is then evaporated to complete dryness and cut into 1- to 1.5-mm cubes. These cubes are placed in a wide-mouth glass-stoppered reagent bottle, and by shaking with a rotary motion the cubes are rounded off and pellets of 1- to 1.5-mm. diameter are obtained. Pellets and powder are separated by sifting; the powder may be used over again by moistening it with distilled water to form a paste which is dried and cut into squares as before. The reagent is stored in a tight-stoppered, wide-mouth reagent bottle. A good grade of granular commercial peroxide^{82, 120} should be dark brown in color and neutral to litmus paper. Small amounts of sodium silicate ("water glass") may be used as a binder.

*Silver Wool.*³ No. 34 silver wire is wound loosely around a glass rod 2 to 3 mm. thick until a roll of silver wire 3 to 4 cm. long and 6 to 7 mm. in diameter has been obtained. Four to five grams of silver wire

will yield several of these rolls, or sufficient for one combustion-tube filling. It is advisable to reduce the silver wire in an atmosphere of hydrogen at about 400° C. in a clean combustion tube and then to heat it once more at the same temperature in a current of oxygen. Previously used silver wire is regenerated in the same manner.

*Platinum Gauze.*³ A piece of platinum wire gauze of 52 to 80 mesh, measuring 3 by 5 cm., is rolled, or fastened with a silver wire if necessary, to form a cylinder of 7-mm. diameter and 3-cm. length. To clean the platinum wire gauze it is boiled several times in dilute nitric acid (1 : 1), washed with distilled water, and ignited to white heat in the non-luminous flame of a Tirrill or Bunsen burner. A previously used platinum wire gauze is regenerated by boiling in dilute hydrochloric acid (1 : 2), dipping in distilled water to remove the hydrochloric acid, then boiling in dilute nitric acid (1 : 1) and igniting to white heat. To facilitate the handling of the platinum wire gauze when cleaning it, a small wire loop is attached to one end.

*Platinized Asbestos (30%).*³ A weighed amount of platinum scrap (old boats, electrodes, unusable wire gauzes, etc.) is dissolved in aqua regia (1 part of nitric acid and 3 parts of hydrochloric acid by volume). A calculated amount of asbestos is added to the resulting solution and the mass evaporated to dryness on a steam bath. The residue is then transferred to a porcelain crucible and ignited in an electric furnace at a temperature of about 1000° C. Prolonged heating, at least ten hours, is necessary to free the platinized asbestos thus prepared from volatile matter.

*p-Cymene.*³⁴ If the boiling point of this substance is not within 175–178° C. it should be redistilled and only the fraction having the above boiling-point range should be used.

Krönig's Glass Cement. It is prepared by melting and mixing 1 part of white beeswax with 4 parts of rosin and casting it in sticks about 10 cm. long and 6 to 7 mm. in diameter which are stored in suitable test tubes.

Testing the Apparatus

Wiping and Weighing of the Absorption Tubes. Incorrect wiping and weighing of the absorption tubes may lead to weighing errors of sufficient magnitude to render the analysis worthless. It is therefore necessary to practice this procedure until constancy of weight of the absorption tubes can be reproduced. As the first step the capillary constrictions of the counterpoised absorption tubes are cleaned with a thin cotton wad twisted around the knurled end of the iron wire. The surface of the water absorption tube, while the tube is held in one hand with a

folded clean and dry chamois at somewhat below the middle, is wiped with the folded moist flannel with a gentle rotary motion from the middle of the tube toward the capillary end, and then in an identical manner with a clean and dry chamois leather until the chamois glides smoothly over the surface of the absorption tube; three such wipings with the chamois are generally sufficient. The position of the water absorption tube is then reversed, the wiped part is held with a chamois, and the other half of the tube is wiped first with the moist flannel and then three times with the chamois. The water absorption tube, which is always wiped first, is placed on the rack provided for it, and the carbon dioxide absorption tube is wiped in an identical manner and also placed on the rack. The rack is placed next to the balance on an asbestos board or cardboard. The purpose of placing the absorption tubes next to the balance immediately after wiping is to allow them to come to equilibrium with the temperature prevailing near or within the balance case. While this equilibrium is attained, which requires from ten to fifteen minutes, the zero reading of the balance is determined, because approximately fifty-five minutes will elapse between the weighing before and after the combustion and the zero reading may change sufficiently during the interval to cause an appreciable error in the result if not taken into consideration.

The water absorption tube is placed on the hooks of the left-hand pan of the balance by means of the wire fork ten minutes after having been wiped. The doors of the balance are closed, and, to save time, the rider on the beam is placed in the notch corresponding to the weight of the absorption tube, so that one may proceed with the weighing of the tube immediately after the fifteen minutes since the wiping have elapsed. The water absorption tube is weighed within ± 0.01 mg. if a micro-analytical balance is used, or within ± 1 deflection unit if an ordinary analytical balance is employed. The water absorption tube is then replaced by the carbon dioxide absorption tube, which is weighed immediately and with the same accuracy. The water absorption tube is then placed on the balance once more and weighed again; the result should check within ± 0.01 mg. with the weight previously obtained. The carbon dioxide absorption tube is also weighed a second time in the same manner. These duplicate weighings may be dispensed with once sufficient experience in the procedure of wiping and weighing has been acquired.

Because the absorption tubes attain constancy of weight approximately ten minutes after wiping and retain this equilibrium for about thirty minutes, the weighing of both absorption tubes should be carried out within twenty to twenty-five minutes. It is important that they

always be weighed in the same order, that is, the water absorption tube first and then the carbon dioxide absorption tube; furthermore, since the time schedule of weighing them must be strictly observed, timing of the weighings with the stop watch is recommended. Occasionally it seems rather difficult to obtain constancy of weight, even though all the conditions stated above have been complied with. This difficulty often can be traced to the accumulation of electrostatic charges on the absorption tubes, especially on dry or cold days. A test for the presence of such charges is performed by bringing the capillary end of the absorption tube near a small piece of tissue paper suspended from a silk thread, which, if an electrostatic charge is present, will be either attracted or repelled. To dissipate such charges the two ends of the absorption tube are touched simultaneously with a metal wire.

Blank Test on the Aspirator. Aside from the constancy of weight of the absorption tubes during a series of weighings it must be possible to reproduce their weight within the allowable limit of deviation (± 0.01 mg. if a microanalytical balance is used, or within ± 1 deflection unit if an ordinary analytical balance is employed) after they are wiped again. Such an experiment is carried out on the aspirator as follows: The absorption tubes after being weighed are connected glass-to-glass and head-to-head, that is, with the ground-glass stoppers facing each other,* with rubber connection II, so that the arrow which indicates the direction of the flow of the gases points toward the carbon dioxide tube. Rubber connection I is attached to the free end of the water absorption tube, with the arrow pointing toward the absorption tube, and then connected to the capillary end of the Anhydrone-Ascarite tube of the aspirator.† The free end of the carbon dioxide absorption tube is attached to the rubber connection of the safety tube of the Mariotte flask. Then the side arm of the Mariotte flask is lowered until a delivery of 8 to 10 ml. of water per minute is obtained. (The aspirator should

* The absorption tubes are always connected head-to-head; disregard of this arrangement necessitates refilling the misplaced absorption tube. The combustion products are mainly absorbed at the entrance, and consequently, if reversed, some of the absorbed combustion products would be swept out or into the adjoining tube. Subsequent reversal to the correct position then produces the same effect, and hence it is impossible to restore the original equilibrium in the absorption tubes.

† Should the rubber tubings adhere too tightly to the absorption tubes they are lubricated with a trace of glycerin applied to a cotton tuft wound around the knurled end of the iron wire, which is then passed through the bore of the rubber connection. All excess glycerin is removed by wiping out the bore with a dry cotton wad. In general, rubber connection II requires lubrication about every fifth determination, and rubber connection I, owing to its proximity to the heating unit, about every second or third determination.

be tested for tightness of the connections at this time by pinching the rubber tubing leading from the wash bottle to the aspirator tube, a manipulation which should stop the flow of water from the Mariotte flask; a loose connection will aspirate atmospheric vapors still containing moisture and carbon dioxide, and this will cause an appreciable increase in the weight of the absorption tubes.) Fifty milliliters of air is passed through the absorption tubes, after which the stopcock on top of the Mariotte flask is closed and the absorption tubes are disconnected from the aspirator. Rubber connections I and II are removed and placed in a Petri dish. Next, the capillary constrictions of the absorption tubes are cleaned with a tuft of cotton and then they are wiped and weighed in the same order and with the exact observance of the same time schedule as before. The result should check within ± 0.01 to 0.02 mg. on a microanalytical balance and within ± 1 to 2 deflection units on the ordinary analytical balance. If a greater deviation is observed, the experiment should be repeated until the proper technic of wiping and weighing the absorption tubes has been acquired.

Blank Combustion Tests. The blank determination serves the purpose of giving assurance of a satisfactory condition of the set-up, particularly a new one, and furthermore is a means of detecting sources of errors or defects either inherent or developed during the use of the apparatus. It is performed on a heated combustion train, that is, the preheater, electric furnace or long burner, and the microburner under the heating mortar are lighted or turned on. The absorption tubes are wiped and weighed as described before and connected head-to-head with rubber connection II to form a glass-to-glass connection. Rubber connection I is attached to the free end of the water absorption tube, which is attached glass-to-glass to the capillary end of the combustion tube, and the free end of the carbon dioxide absorption tube is joined to the safety tube of the Mariotte flask.

The flow of oxygen through the system is standardized to the correct combustion conditions by adjusting the pressure regulator to a head of about 5 cm. and then lowering the side arm of the Mariotte flask to a horizontal position. As soon as bubbles rise outside the jacket of the pressure regulator, the stopcock on top of the Mariotte flask is opened. Water will begin to drip from the side arm; after a few seconds, or when the flow has become regular, it is measured in a 10-ml. graduate cylinder and timed with a stop watch. The correct pressure in the system, as measured by the displacement of water in the Mariotte flask, is reached when a discharge of 5 ml. of water per minute has been obtained. To increase the rate of flow of oxygen through the system, the jacket of the

pressure regulator is depressed, or, if the difference is very slight, the side arm of the Mariotte flask is lowered; to decrease the pressure in the combustion train the head in the pressure regulator is reduced, or the side arm of the Mariotte flask raised. At no time, however, should the side arm be off more than a few degrees from its horizontal level; the pressure should be regulated principally by the pressure regulator and only the finer adjustment is made by manipulating the side arm of the Mariotte flask.

An additional means of calibrating the volume of oxygen passing through the system per minute is provided by the bubble counter by counting the number of bubbles rising from the aperture during a given time—10 seconds for instance—after the correct pressure has been established. Subsequent countings, taken at any time, either before a combustion is started or during the combustion itself, should then give assurance that pressure conditions are normal if the same count is obtained, or call attention to a fluctuation or possible disturbance in the event of a deviation. One hundred and fifty milliliters of oxygen is passed through the combustion train at the rate of 5 ml. per minute, after which the stopcock on top of the Mariotte flask is closed and the absorption tubes disconnected from the combustion train and immediately attached to the aspirator. About 50 ml. of air is drawn through the absorption tubes at a rate of 7 to 10 ml. per minute, and then they are detached from the aspirator and their capillary constrictions cleaned with a cotton tuft. They are wiped and weighed as before, and the increase in weight should be less than 0.04 mg. for the water absorption tube and 0.02 mg. for the carbon dioxide absorption tube if the apparatus is in satisfactory condition and the wiping and weighing have been performed properly.

The sources of error responsible for undue increases in weight of the absorption tubes are usually directly traceable to bad connections and leakages in the system, poor-quality rubber tubing, excessively lubricated rubber connections, or the filling of the combustion tube, U-tube, and also the absorption tubes. Since errors due to improper filling of the absorption tubes can be detected when air is passed through them on the aspirator, and the U-tube containing Ascarite and Anhydron seldom is responsible for errors, unless the described arrangement of the filling has been entirely disregarded, only the rubber connections and the combustion tube remain to be tested. Of the rubber connections only the two used for the attachment of the absorption tubes may prove troublesome if not properly impregnated, or if excessively lubricated, or if the combustion is carried out under abnormal pressure conditions; the rubber connections on the combustion train should not give rise to

any difficulties if a preheater is employed and all the connections between the preheater, bubble counter, and combustion tube are made glass-to-glass.

Whether the increase in weight in either one or both absorption tubes is due to the reagents in the purifying train (U-tube and the two Anhydrone tubes), or is traceable to the filling of the combustion tube, can be determined by running one blank on an unheated apparatus, with only the preheater lighted, and a second blank with the regular heating devices lighted or turned on. If the absorption tubes show undue increases in the first blank, the reagents of the purifying train can be held responsible and must be renewed; if, however, an increase is noted only upon heating the apparatus, the filling of the combustion tube is at fault. Of the reagents comprising the filling, the lead peroxide is likely to be the most troublesome, especially as far as the hydrogen values are concerned, owing to its characteristic of retaining water and then giving it off slowly over a prolonged period of time. Experimental observation has shown that the lead peroxide of a new combustion-tube filling gives off traces of water even after several hours of heating. The same observation can be made whenever the apparatus is heated after having been idle for some time. Heating out the apparatus for several hours while passing oxygen through at a rate of approximately 5 ml. per minute will, as a rule, remedy this fault. Should the high hydrogen values persist in spite of this treatment, it is best to refill the combustion tube with lead peroxide of a purer grade. A high-hydrogen blank may also be due to the hygroscopic properties of the rubber connections between the water absorption tube and the combustion tube, but this can readily be detected by placing them in a desiccator over a dehydrating agent several hours before the blank determination, although this rigorous dehydration should not be resorted to normally, because then a low hydrogen value would be the result. Should the carbon dioxide tube show a persistent gain in weight (more than 0.02 mg. during a blank determination), impure or improperly ignited copper oxide or platinized asbestos may be at fault.

Actual Analysis

After completion of a satisfactory blank determination, an analysis of a pure, known substance such as resorcinol, benzoic acid, or azobenzene is carried out. When correct results have been obtained the apparatus is ready for the analysis of unknown compounds or research substances. It is advisable, however, to continue to combust a few more compounds of different molecular structure, liquids as well as solids, containing also other elements, and varying in percentage composition

of carbon and hydrogen, in order to study the behavior of different types of compounds upon combustion.

PREPARATION OF THE SAMPLE

Solids. The substance is weighed in a platinum boat which previously has been cleaned in the usual manner. Special weighing procedures (for hygroscopic substances, semi-solids, syrups, fats, waxes, etc.) are described in detail on p. 48.

Liquids. Liquid substances are weighed either in weighing pipets or, if the sample is not hygroscopic or volatile, in the platinum boat. The weighing pipet which contains a little potassium chlorate, is filled with the substance and weighed as described on p. 46. (Since the filling and weighing of the pipet are more time-consuming than the weighing of a solid substance, it is advisable to fill and weigh all the pipets for a series of determinations before the analyses are started.) Before being introduced into the combustion tube the pipet is again centrifuged, its tip broken off, and then placed in a previously cleaned platinum foil with the open end of the pipet facing the heating unit.

COMBUSTION

Attaching the Absorption Tubes. The weighed absorption tubes are connected head-to-head and glass-to-glass and then so attached to the combustion train that the free end of the water absorption tube is connected glass-to-glass to the capillary end of the combustion tube and the free end of the carbon dioxide absorption tube is joined to the safety tube of the Mariotte flask. The stopcock on top of the Mariotte flask remains closed for the time being.

Introduction of the Sample. During the introduction of the substance, the stopcock on top of the Mariotte flask remains closed to build up pressure in the system so that when the cork stopper is removed from the mouth of the combustion tube oxygen will escape rather than air be drawn into it. The sample is transferred to the combustion tube as follows: The stopper is removed and placed on the glass top of the dessicator; next, the metal block with the sample is raised to the mouth of the combustion tube, the platinum boat or foil is introduced with clean forceps and pushed with a clean glass rod within 5 cm. of the heating unit; then the combustion tube is closed tightly with the stopper.

Combustion of the Sample. The side arm of the Mariotte flask is lowered to a horizontal position, its stopcock opened, and the displacement of water by the oxygen passing through the system is measured and standardized to a flow of 5 ml. per minute, as described in the blank determination. The combustion is started about 5 cm. in front of the

platinum boat or foil with a non-luminous slightly hissing flame 5 to 6 cm. high or high enough to extend about 2 cm. above the wire gauze of the combustion tube. The burner is gradually moved toward the substance and it should be noted whether it distills, sublimes, or chars. If the substance distills or sublimes, the ring of distillate or sublimate is slowly driven toward the heating unit. Substances which decompose with charring often require prolonged heating directly under the boat until all organic matter is burned off. The combustion is carried out with 75 ml. of oxygen passing through the system, as measured by its equivalent volume of water collected in a 250-ml. graduate cylinder, which, at the start of combustion, is placed under the side arm of the Mariotte flask. The combustion requires about fifteen minutes, divided approximately as follows: five minutes of heating to reach to sample, five minutes of heating directly under it, and five minutes to heat the intervening space from the sample to the heating unit. Explosive or difficultly combustible substances may require suitable modification of the combustion, but, nevertheless, the total time of fifteen minutes should not be greatly exceeded. Then the combustion is repeated, only more rapidly, again starting about 5 cm. in front of the platinum boat or foil; this second combustion requires about five minutes and is distributed by heating about one and one-half minutes to reach the platinum boat, two minutes of heating directly under it and one and one-half minutes to heat the combustion tube from the platinum boat to the heating unit. The movable gas burner is extinguished and the gaseous combustion products are swept into the absorption tubes for twenty minutes with 100 ml. of oxygen, thus requiring a total of about forty minutes for the entire combustion. During the forty minutes 200 ml. of oxygen will have passed through the combustion train and its equivalent volume of water collected in the graduate cylinder. Measuring the displacement of water by the oxygen in the Mariotte flask and comparing it with the time elapsed during the combustion affords a very accurate means of observing the smooth progress of a determination. Occasionally stoppages occur during the combustion; these are mainly due to condensation of water in the capillary constrictions of the water absorption tube, and the difficulty is remedied by applying the heated end of a metal rod or file to the affected constrictions.

After the sweeping out of the gaseous combustion products the stop-cock of the Mariotte flask is closed, but its side arm is left undisturbed in the horizontal position, which eliminates the necessity of restandardizing the flow of oxygen at the beginning of the next determination. Once regulated, the pressure in the system will remain unchanged for an entire series of analyses.

Removal of the Absorption Tubes. The absorption tubes are removed from the combustion train and immediately attached to the aspirator without disconnecting them from each other; the free end of the water absorption tube is connected to the Ascarite-Anhydrone tube and the free end of the carbon dioxide absorption tube is attached to the safety tube of the Mariotte flask. Fifty milliliters of air is drawn through the system at a rate of 7 to 10 ml. per minute and measured by the displacement of water in the Mariotte flask. The absorption tubes are then removed from the aspirator and the capillary constrictions wiped with a clean cotton tuft. Finally, they are wiped, placed near the balance on a rack, and weighed after fifteen minutes as described on p. 123.

Rubber connections I and II are placed in a Petri dish, but on very humid days it is better to place them in a desiccator containing a weak desiccant such as calcium chloride.

It is advisable to time the individual steps of an analysis with a stop watch, especially when running a series of determinations. A time schedule, beginning with the wiping of the absorption tubes, is given below:

| Time: | Minutes |
|---|---------|
| Wiping of the absorption tubes..... | 5 |
| Taking the zero reading of the balance..... | 5 |
| Waiting until absorption tubes become constant (15 minutes from time of wiping)..... | 10 |
| Weighing the water absorption tube..... | 5 |
| Weighing the carbon dioxide absorption tube..... | 5 |
| Reweighing both tubes..... | 10 |
| Attaching the absorption tubes to combustion train, introducing sample, standardizing the flow of oxygen | 5 |
| First combustion..... | 15 |
| Second combustion..... | 5 |
| Sweeping out the combustion products *..... | 20 |
| (During this time the sample for the next analysis is weighed) | |
| Removing the absorption tubes from the apparatus and attaching them to the aspirator and passing through 50 ml. of air..... | 10 |
| Wiping and weighing the absorption tubes..... | 40 |
| Total..... | 135 |

* The sweeping-out period given above as twenty minutes should be extended to thirty minutes if water in an amount exceeding 2.5 mg. is collected and if a *combination band* combustion-tube filling has been used for this particular determination.

Calculation:*Percentage of Hydrogen:*

Log of weight of water,
 Plus log of factor (04875),
 Plus negative log of weight of substance;
 Antilog of total = percentage of hydrogen.

Percentage of Carbon:

Log of weight of carbon dioxide,
 Plus log of factor (43600),
 Plus negative log of weight of sample;
 Antilog of total = percentage carbon.

Remarks**DRY COMBUSTION METHOD**

The outstanding features of F. Pregl's ^{106a, 113} micromethod for the determination of carbon and hydrogen are:

- (a) reduction of the size of the sample to a few milligrams,
- (b) the saving of time, and
- (c) perfect volume and pressure control.

Since the introduction of this method in organic elementary analysis in 1912 a large number of investigators ^{19, 25, 28, 33, 35b, 39, 41, 42, 75-78, 81, 88, 90-98, 115, 123, 124, 128, 132, 143-146} have studied and repeatedly reviewed this most important of all analytical methods in organic chemistry.

ACCURACY

The accuracy obtainable in this method depends upon the procedure employed and the skill and experience of the operator. The following claims have been made:

- $\pm 0.1\%$ by A. Friedrich; ^{41f}
- $\pm 0.1-0.2\%$ in F. Pregl's laboratory; ⁷⁵
- $\pm 0.2\%$ by A. Elek, ^{35a} D. F. Hayman, ⁵¹ and R. Roth; ¹¹²
- $\pm 0.3\%$ general average. ¹¹³

On the average, particularly when the apparatus is used by several non-expert operators, as in a laboratory course, it can be stated that the accuracy obtainable in the micro carbon and hydrogen determination is about the same as in the corresponding Liebig macro combustion method, ³⁸ i.e.:

Allowable error (0.2-gram sample).

Carbon, 5 parts per thousand.

Hydrogen, 30 parts per thousand.

This statement appears also supported by F. W. Power¹⁰⁴ in calculations from statistical analysis data obtained from actual micro combustion analyses performed by several analysts in different laboratories. The above-given accuracy, however, must not be compared with atomic-weight determination for carbon by combustion analysis, in which a special apparatus and painstakingly purified substances in the amount of 1 to 3 grams were used.^{9, 10, 37}

APPARATUS

Oxygen Tank. The previously used gasometers^{106a, 113} have been replaced by an oxygen tank provided with suitable pressure-reduction valves. In regard to the oxygen used in the combustion it is necessary that it be free of organic impurities.^{41b, 57} If a preheater is incorporated in the ante-combustion train, the purity and consequently the source of the oxygen, whether electrolytic oxygen or oxygen obtained by fraction distillation, is of little importance, because any combustible matter present in the oxygen stream is combusted to carbon dioxide and water, respectively, and consequently absorbed by the purifying train. The necessity of purifying both oxygen and air used in the combustion has been emphasized by a number of investigators.^{18, 22, 97}

Preheater. The preheater of F. Böck and K. Beaucourt¹⁸ fulfills this requirement admirably. It was improved by making the spiral tube detachable.⁹⁸ Thus a Pyrex or soft-glass spiral tube possessing a standard ground-glass joint can be used and only the vertical short combustion tube needs to be of quartz or Supremax glass. A horizontal short combustion tube⁵¹ or a simple copper spiral⁸⁰ may be employed as a preheater, but care must be taken to protect the rubber attachments from heat. Combustion in oxygen only has been found suitable by many investigators.^{41, 51, 65, 83, 97, 114, 126, 139, 147} Medicinal oxygen may be used without a preheater.^{35, 114}

If the preheater is omitted from the ante-combustion train, the rubber tubing connecting the various parts of the apparatus must be specially prepared or aged, and a number of directions in regard to such treatment have been given by several investigators. F. Pregl^{106a, 113} suggests the heating of the rubber tubing at 100 to 110° C. for several hours while air passes through the tubing. The treatment of rubber tubing with strong potassium hydroxide on a steam bath,^{41b} or steaming out until the tubing is odorless, has been suggested as another remedy. M. Boetius^{18a} and J. Lindner^{77, 78} minimize the rubber tubing used in the ante-combustion train as a source of error.

Pressure Regulator. The original simple pressure regulator described in this manual has been retained by most investigators; the attachment

of a drying tube to the outlet of the pressure regulator has been found advantageous.^{19b, 97} A pressure regulator based upon the principle of measuring gas velocity¹⁰⁸ has been described by A. Friedrich^{41d} and others.^{49, 77, 78, 112, 135} The apparatus consists of horizontal thick-walled capillary tubing with two stopcocks provided with edgings for precise adjustment. A capillary U-tube, half filled with colored paraffin oil, is sealed to the horizontal flow tube in such a way that one arm of it is situated between the two stopcocks. The pressure existing in the system is read on a scale which shows the difference in the niveau of the two menisci of the paraffin oil. The use of a gas reduction valve for flow control has been advocated by J. Lindner,^{77, 78} while W. H. Hamill⁴⁹ and J. E. Vance¹³⁵ proposed the use of a manometer for the same purpose.

Bubble Counter and U-Tube. The original form of the combined bubble counter and U-tube has been generally retained, although an enlarged type is usually preferred.⁹⁷ Modified devices for a similar purpose^{19b} as well as complete omission^{41c} of this convenient gas flow indicator have been proposed.

Combustion Tube. Changes in the dimension and size of the combustion tube for micro work have been proposed only in one instance.³⁹ Combustion tubes made of transparent quartz or Supremax glass are preferred. Metal combustion tubes have also been suggested.⁵ Attachment of a side arm to the combustion tube has been suggested by E. Müller and H. Willenberg⁸³ and has by now been universally adopted.^{79, 97}

Combustion-Tube Fillings. The so-called *universal* combustion-tube filling suggested and employed by F. Pregl^{106, 113} was the subject of a number of investigations, notably by M. Boetius,¹⁸ C. Weygand,^{143, 144} and J. Lindner.^{77, 78} All possible sources of errors have been investigated and advice about overcoming them has been given.

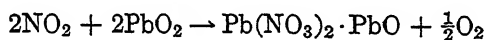
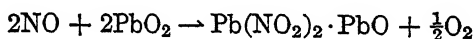
The asbestos used in combustion-tube fillings was found to be least responsible for disturbances, except that it has the tendency to swell upon heating, thereby affecting the velocity of the gas flow. The swelling may increase the volume of the asbestos by as much as 70%, a fact which has to be taken into consideration when filling the combustion tube.

The copper oxide, which may be activated,¹¹⁹ has to be examined for basic and volatile constituents; the former can be removed by treatment with acetic acid, followed by strong ignition in open air. The use of lead chromate in combustion-tube fillings has been discontinued.^{95, 114}

Commercial silver wool, which has been found to be an adequate absorbent not only for halogen but also for the oxides of sulfur, is usually

satisfactory. Possible traces of grease are removed by heating. The silver wool may be replaced with electrolytically prepared finely divided silver powder.⁸⁰

The most serious source of error is the lead peroxide,^{9, 28, 41, 46, 66, 142-144} and consequently the directions given by F. Pregl^{106a, 113} for its preparation must be followed implicitly. M. Boetius^{19c} carried out a number of experiments in regard to the absorption and elimination of water from this reagent and finally recommended the combustion of a substance high in hydrogen content from time to time to re-establish equilibrium. Granular lead peroxide is preferred. A. Friedrich^{41d, e} finds that carbon dioxide is also gradually absorbed by the lead peroxide and then given off again when substances containing nitrogen, halogen, or sulfur are combusted. The mechanism of the absorption by lead peroxide of the various oxides of nitrogen formed during the combustion of nitrogen-containing substances has been studied by W. R. Kirner,⁶⁵ who showed that the absorption proceeds in accordance with the following equation:



Complete elimination of the lead peroxide from combustion-tube fillings by substituting metallic copper,^{33, 98} or silver,⁶⁹ or "Hopcalite"²⁸ has been attempted.

In this manual four combustion-tube fillings have been described, i.e.: a *simple* and a *combination* filling and a *simple band* and a *combination band* filling. Use of the simple combustion-tube filling is indicated in teaching, where the choice of the sample is up to the instructor. This type of combustion-tube filling is applicable to any substance *not* containing nitrogen; it has the advantage that it does not contain lead peroxide, and consequently all disagreeable features of this reagent are eliminated. The simple band filling is necessary when substances of the sterol group, or substances possessing highly condensed ring systems with angular alkyl groups, have to be analyzed. These types of substances invariably gave low results when analyzed with the F. Pregl^{106a, 113} so-called *universal combustion* tube filling. The other two fillings are adaptations of the simple and the simple band fillings to organic substances containing nitrogen, when the use of lead peroxide becomes necessary.

The introduction of gold wire into the combustion tube becomes necessary in the combustion of substances containing mercury.^{45, 56, 138}

The influence of other elements has been studied by F. C. Silbert and W. R. Kirner¹²⁶ and by H. Roth.¹¹²

Radical changes in the combustion-tube filling have been proposed by P. Haas and F. Rappaport⁴⁷ and by G. Ware-Wellwood,¹⁴¹ who suggested the use of cerium dioxide. P. L. Kirk and A. McCalla⁶³ recommend manganese dioxide for the same purpose. It is claimed that by the use of this reagent the life of the combustion tube is considerably prolonged. The use of platinum, either as gauze or in the form of platinized asbestos, and the use of palladium asbestos⁶⁵ have been found advantageous.

Absorption Tubes. The weighing errors caused by various influences (humidity, changes in atmospheric pressure, use of various types of tares, etc.) upon absorption tubes have been repeatedly investigated.^{19, 36, 41f, 51, 56, 77, 78, 104, 111, 121, 128, 137, 143} The original absorption tubes as devised by F. Pregl^{106a, 113} and as standardized by H. Lieb and A. Soltys⁷⁴ have been found entirely satisfactory, particularly when used with an aspirator.⁹⁷ If the precision absorption tubes as recommended by the latter are not available, the introduction of fine metal wires (copper) into the capillary constrictions during the weighing period is of decided advantage,^{19e, 97} particularly in humid weather. The use of a control absorption tube was suggested by A. Friedrich,^{41f} while J. B. Niederl and E. M. Livingstone⁹³ recommend the use of a *tare* absorption tube to minimize the influence of unfavorable atmospheric conditions.

The formation of electrostatic charges on the absorption tubes during the wiping process in dry weather is observed very frequently, and several remedies which include the use of ultraviolet light,¹¹¹ or a high-frequency discharge,¹³⁷ or the drawing of the absorption tube through a flame¹²⁸ have been suggested. It was found that a humidity of 60 to 70%,⁵¹ which can easily be maintained in any laboratory, is desirable. Absorption tubes made of Pyrex glass cannot be used.

The use of *Anhydron*⁷ (magnesium perchlorate) for the absorption of water has been widely adopted,⁹⁷ although calcium chloride,^{106a, 112} Dryerite (anhydrous calcium sulfate),^{35, 50} as well as phosphorus pentoxide^{19d, 32, 134} are still in vogue. Similarly, *Ascarite*¹³¹ (solid sodium hydroxide on asbestos) has replaced⁹⁷ the soda-lime^{106a, 113} used previously.

The use of a double set of absorption tubes has been found of advantage in series of carbon and hydrogen determinations.⁹⁷ Absorption tubes provided with ground-glass joints, thus obviating the use of rubber connections, have been described by K. Bürger²³ and G. L. Royer and co-workers.¹¹⁴

For combustion procedures in which the temperature and pressure conditioning *aspirator*⁹⁷ is omitted, sealable absorption tubes have repeatedly been proposed. The first of these types were the vertical absorption tubes of F. Blumer,¹⁶ which were subsequently improved by J. V. Dubsky,³³ B. Flaschenträger,³⁹ K. Lindenfeld,⁷⁶ and others.¹³⁴ G. Kemmerer and L. T. Hallett⁶⁰ suggested horizontal absorption tubes provided with a mercury seal. These types of tubes were subsequently improved by R. T. K. Cornwell²⁷ and R. J. Robinson and D. J. Doan.¹¹⁰ Successful replacement of the mercury seal by steel ball valves was reported by I. B. Johns.⁵⁹ Several types of mechanically sealable absorption tubes have been described by A. Friedrich.^{41c, f} Of these the one designed by E. Abrahamczik¹ proved most successful and has been repeatedly studied.^{26, 105} R. O. Clark and G. H. Stillson²⁶ have enlarged the Abrahamczik types of absorption tubes. These types of absorption tubes have to be opened to the atmosphere for the equalization of pressure, and only when counterpoised with a similar absorption tube do they show greater constancy in weight than the open Pregl absorption tubes^{106a, 113} used without an aspirator. "Lefcoseal" stopcock grease is used to lubricate the ground-glass joint.

Rubber Tubing and Connections. The heavy-walled rubber tubing employed for the connections between the absorption tubes has to be specially aged.^{41, 106a, 113} The hygroscopicity of this type of rubber tubing has been found to be considerable, and storage in a desiccator of phosphorus pentoxide has therefore been recommended.¹³

Heating Mortar. The original heating mortar as devised by F. Pregl,^{106a, 113} underwent a number of changes and improvements.^{72, 138} At present the all-glass heating mortar of A. Schöberl⁷² seems to incorporate all the advantages of previously designed devices. Scores of electrically heated heating mortars have been devised and are on the market.^{61, 62, 117, 122}

Mariotte Flask. The Mariotte flask for measuring the volume of the combustion gases has been improved by the introduction of a stopcock^{68, 97, 133} and automatic refilling devices,⁶ and has been retained by most investigators.^{68, 97, 133}

Heating Units. The long burner has been superseded by equivalent electric heating devices of various designs.^{3, 39, 44, 48, 84, 117} Electric furnaces with platinum wiring and movable in all directions³ have been found very practical. For heating the sample an ordinary gas burner, which allows close observation of the combustion process, is preferred, although replacement of this burner by electric heating units^{61, 62, 117, 122} with automatic movements^{48, 62, 107, 114} has been proposed.

TREATMENT OF THE SAMPLE

The directions for the preparation and the weighing of the sample, which *must* be a *pure* organic compound, as otherwise the analytical results become meaningless, have been given under the appropriate chapter; they include directions for solids (p. 42), liquids (p. 46), and hygroscopic substances (p. 48). Experiences and directions for carrying out a large number of analyses have been described by M. S. Sherman and R. T. Milner,¹²⁵ while C. Tiedcke¹³² stated directions and precautions for the analysis of explosive substances. For substances which sublime easily the "technic of the two boats"^{36b} is employed to advantage. Novel calculation tables for the direct calculation of the carbon and hydrogen content of organic compounds have been devised by Y. Asahina and S. Bannai.⁴ Experience with the Pregl micro carbon and hydrogen apparatus in the tropics has been related by M. C. Nath.⁸⁸

MODIFICATIONS

A *catalytic dry combustion* method following the principle of M. Dennstedt³⁰ was devised by A. Friedrich.^{41e} The combustion is carried out in oxygen, and the lead peroxide is placed in two separate boats. This procedure has the advantage that the lead peroxide may be readily exchanged when exhausted. In this method, a platinum contact, 10 cm. long and 5 cm. wide and folded to form a spiral, serves as a catalyzer in the oxidation. The exclusive use of oxygen, without employment of an aspirator, necessitates sealable absorption tubes.^{1, 41c, f} An asbestos plug, introduced at the end of the combustion tube, serves for the establishment of the excess pressure necessary during the combustion. The danger of incomplete combustion nevertheless exists, necessitating suitable changes in the combustion procedure, such as inverted slow combustion of the substance.

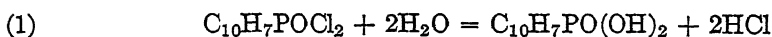
Combustion in an *atmosphere of nitrogen* without the use of lead peroxide was studied by J. B. Niederl and J. B. Whitman,⁹⁸ who mixed the substance with an excess of finely powdered copper oxide to achieve complete combustion.

A dry combustion method in which the carbon is determined gravimetrically in the form of *barium carbonate* has been described by J. B. Niederl and J. R. Meadow.⁹⁴ The combustion gases are passed into a suitably constructed filter absorption tube. The barium carbonate precipitate is filtered in a closed system under exclusion of the atmosphere and is then dried and weighed as usual. This method is too complicated for everyday use, but it permits finer differentiation in the carbon values and reduction of the amount of sample used for analysis to 0.5 mg.

or less. Two-tenths of a milligram of substance could still be analyzed quantitatively by this method to within $\pm 1\%$.

A *titrimetric dry combustion* method for the determination of *carbon* has been devised by R. B. Schmitt and J. B. Niederl¹²¹ and by R. H. Nagel.⁸⁵ A suitably constructed absorption-titration vessel, provided with a spiral gas-inlet tube and an automatic drain arrangement,⁸⁵ is attached to the usual combustion tube. Into the same vessel extend the capillary delivery tubes of the 0.1 *N* barium hydroxide solution, an excess of which is used for the quantitative absorption of the carbon dioxide, and the 0.05 *N* acid hydrochloric acid, which is used for the back titration of unused alkali. The gas-outlet tube of this titration vessel is attached to a Mariotte flask in the usual manner, and consequently the combustion, absorption, and titration are carried out in a closed system.

A *titrimetric dry combustion* method for the determination of both *carbon and hydrogen* has been described by J. Lindner.^{77, 78} The hydrogen is determined as hydrogen chloride, formed by the interaction of the water formed in the combustion with naphthyl phosphorus oxychloride as follows:



Each molecule of water thus forms two molecules of hydrogen chloride, corresponding to the formation of one mole of hydrogen chloride for each hydrogen atom. The hydrochloric acid formed is determined titrimetrically. The carbon dioxide is absorbed in an excess of 0.1 *N* barium hydroxide solution, and the unreacted alkali is titrated back with 0.05 *N* hydrochloric acid solution.

A dry combustion method for the simultaneous determination not only of carbon and hydrogen but also of oxygen has been described by W. R. Kirner⁶⁵ and others.^{53, 77, 78, 134}

WET COMBUSTION METHODS

H. Lieb and co-workers^{73, 118} have devised a *micro wet combustion method for carbon*, which is based upon the earlier macro procedures of M. Nicloux and A. Boivin^{20, 89} and the semi-micro procedure of H. Dieterle.³¹ The substance is oxidized in a solution of potassium and silver dichromate in concentrated sulfuric acid. The resulting combustion gases are further catalytically combusted in a stream of oxygen and then are absorbed in a suitably constructed titration vessel possessing a glass fritter gas distribution inlet tube. For the absorption of

the carbon dioxide an excess of 0.1 *N* barium hydroxide is used, the unused alkali being titrated with 0.05 *N* hydrochloric acid solution. Suitable modification in the oxidation vessel for the introduction of capillaries allows also the combustion of liquid substances.¹¹⁸

A series of somewhat similarly constituted semi-micro wet combustion methods have been devised. In most of them potassium or silver dichromate, or both,^{2, 20, 40, 64, 89, 103} is used as the oxidizing agent. Since this agent alone does not always ensure complete combustion, the combustion gases are usually subjected to a catalytic after-combustion.^{25, 102} Instead of dichromates, potassium permanganate,⁸⁶ potassium iodate,^{25, 127} and persulfate¹⁰⁹ have been suggested as oxidizing agents.

GAS VOLUMETRIC AND MANOMETRIC METHODS

Several types of gas-volumetric methods for the determination of carbon alone^{8, 13, 29, 136} or of carbon and hydrogen and also of simultaneous determination of carbon, hydrogen, and nitrogen,^{11, 15} carbon and oxygen,²⁴ and carbon, nitrogen, and oxygen⁶⁷ have been devised. The procedures may involve dry as well as wet combustion methods, with either volumetric^{8, 29} or manometric¹³⁶ determination of the combustion gases.

In the *manometric wet combustion method* for carbon as devised by D. D. Van Slyke and J. Folch^{136a} the combustion mixture, which effects quantitative oxidation of the sample in one to three minutes, consists of fuming sulfuric, phosphoric, chromic, and iodic acids. The carbon dioxide formed is collected and measured in the Van Slyke-Neill manometric apparatus (Fig. 35, I and II), which consists essentially of a digestion tube, the carbon dioxide absorption chamber, and the manometer. The combustion mixture is prepared by adding 167 ml. of syrupy phosphoric acid (sp. gr.: 1.7) and 333 ml. of fuming sulfuric acid (20% sulfur trioxide) to 25 g. of chromium trioxide (chromic acid anhydride) and 5 g. of potassium iodate contained in a 1-liter Pyrex Erlenmeyer flask provided with a ground-glass stopper. The absorption liquid consists of carbonate-free 0.815 *N* sodium hydroxide solution to which hydrazine sulfate (2 g. for each 100 ml. solution) has been added.

The actual combustion is carried out as follows: Into the digestion tube containing the weighed sample are introduced several pieces of Alundum and 200 mg. of potassium iodate. With a medicine dropper a thick ring of syrupy phosphoric acid is then drawn around the upper part of the ground-glass joint of *T* (Fig. 35, I), while *T* is in a horizontal position. Cup *F* of connecting tube *Q* is filled to the 2-ml. mark with fresh combustion fluid, and the stopper is then fitted to the digestion

tube containing the sample. The digestion tube is now connected with chamber *C*, as shown in Figs. 35, I and II, chamber *C* being completely filled with mercury. Cock *b* (Fig. 35, I) is turned to connect *C* and *T*, and the mercury in *C* is lowered to the 50-ml. mark. This procedure draws about two-thirds of the air from *Q* and *T* over into *C*. Cock *b* is then closed, mercury is readmitted into *C*, the air trapped over the mercury in *C* is ejected through cup *E*, and cock *b* is then closed again.

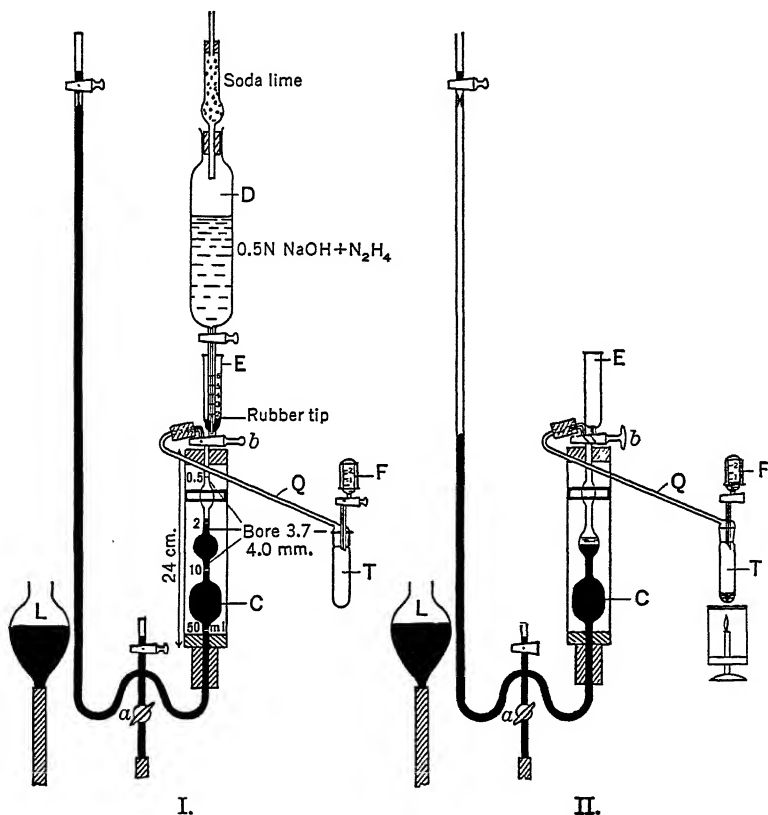


FIG. 35.

After this, 2 ml. of the alkali-hydrazine solution is measured from *D* into *C* through a mercury seal, as shown in Fig. 35, I. The admission of the alkali is best regulated by opening cock *b* wide and controlling the flow of mercury through cock *a*. The admission is stopped when the mercury in *C* falls to a level of about 1 mm. above the 2-ml. mark, as shown in Fig. 35, I. Then *D* is withdrawn and mercury from *E* is let into the chamber to fill the capillaries of cock *b*. The displacement

of the slight volume of solution from the capillary of *b* into the chamber brings the volume of solution in *C* to exactly the 2-ml. mark. Cup *C* is rinsed with acidified water; this cup is never permitted to stand with its walls wet with alkali.

Then *L* is lowered, and mercury is drawn out of *C* and the manometer until the mercury in the manometer is about level with the 2-ml. mark on *C*. Cock *a* is then closed, and cock *b* is turned to connect chamber *C* with the combustion tube. The leveling bulb is then placed, as shown in Figs. 35, I and II, at such a height that the mercury surface in it is about level with the 50-ml. mark on *C* and remains at this level until the combustion is finished. A measured volume of combustion fluid is now run from *F* into *T*; for combustions with 2 to 3.5 mg. of carbon 2 ml. of the fluid is used. The microflame is now brought under the combustion tube, and the arrangement is as shown in Fig. 35, II.

Fine bubbles of carbon dioxide gas begin to rise in the combustion fluid as soon as the fluid is warmed. A minute or so is taken to warm it to boiling. Preferably the evolution of carbon dioxide should not be so rapid that at any time it makes a foam collar more than 2 cm. high on the fluid, although even if it should fill the greater part of the tube, the analysis is not necessarily lost. After the initial carbon dioxide evolution the fluid is heated rapidly to boiling.

As carbon dioxide and oxygen are evolved, the mercury falls in *C* (Fig. 35, I) and rises in the manometer. Cock *a* is slightly opened every few seconds at this stage to admit mercury from *L* into *C* and keep the gas space in *C* at about 1 ml. Within about a minute from the beginning of heating enough gas has been evolved to press the mercury in the manometer up to its top, and to permit complete opening of cock *a* without causing backflow of alkali solution from *C* to *T*. Cock *a* is now left fully open during the rest of the combustion, and the boiling proceeds quietly at about 150 mm. less than atmospheric pressure. Vigorous boiling at about 600 mm. pressure is continued, with foam filling one-third to one-half of the tube, for 1.5 minutes to complete the combustion.

After the combustion is completed, the flame is left under the tube exactly as during the combustion, while the mercury in *C* (Fig. 35, I) is lowered and raised 20 times to cause complete transfer of carbon dioxide to the alkali solution in *C*. The 20 excursions should take about three minutes. At each lowering of the leveling bulb the mercury in *C* is dropped to about the 50-ml. mark, and the fluid in *T* boils vigorously. The tube should then fill with foam. At each raising the bulb is lifted till the gas space in *C* is compressed to about 5 ml. After 5, 10, 15, and 20 excursions of the mercury in this manner, the respective per-

centages of the carbon dioxide transferred to the alkali solution in *C* have been found to be 91, 98.3, 99.7, and 100.

After the absorption is completed, the flame is removed from the combustion tube, cock *b* (Fig. 35, I) is closed, and tube *Q* is disconnected from the chamber. The hot combustion tube is removed with tongs or a strong metal test-tube holder.

Before oxygen and nitrogen are ejected, the curved inlet capillary above cock *b* is filled with mercury drawn in from a small bottle. About as much mercury is left in this capillary above the cock as is shown in Fig. 35, I. Then, with cock *b* closed, the gases in *C* are put under positive pressure by raising leveling bulb *L* a little above cock *b*. With the bulb at this level, cock *a* is closed and *b* opened to connect chamber *C* with cup *E* above it. Mercury is then admitted from *L* into chamber *C* until the rising alkali solution, driving the gases out through *E*, just reaches the bottom of cock *b*. In succession cocks *a* and *b* are then closed. The leveling bulb is lowered to the position shown in Figs. 35, I and II, and a little mercury is admitted from cup *E* into the chamber to seal the connecting capillary. A small bubble of air, trapped in the capillary, is thus readmitted into *C*, but it has no influence on the carbon dioxide determination, since it is free of carbon dioxide.

Exactly 1 ml. of 2 *N* lactic acid is measured into chamber *C* from an accurate stopcock pipet provided with a rubber-ringed tip. The admission is made through a mercury seal in the same manner shown in Fig. 35, I, for the admission of alkali. Mercury to fill the connecting capillary between *E* and *C* is admitted after the acid.

The mercury in the chamber is then lowered to the 50-ml. mark, cock *a* leading to the leveling bulb is closed, and the chamber is shaken twenty or thirty seconds, most of the carbon dioxide being extracted from the solution. The carbon dioxide that has entered the gas phase increases the pressure there enough to force the mercury down below the 50-ml. mark. To correct for this displacement, enough mercury is admitted from the leveling bulb to bring the top of the mercury meniscus in the chamber exactly to the 50-ml. mark. The chamber is then shaken for 1.5 minutes to complete the extraction of the carbon dioxide from the solution.

Mercury is now admitted from the leveling bulb until the volume of the gas phase in the chamber is reduced to 10 ml. As the meniscus of the solution in the chamber approaches this mark it is desirable to watch it with a magnifying lens in order to stop it exactly on the line.

The reading p_1 is then taken on the manometer. After this the cock leading to the leveling bulb is opened, while the bulb is left at the level as shown in Figs. 35, I and II, so that the gas in the chamber is under

slight negative pressure. Into cup *E* is measured 0.5 ml. of 5 *N* sodium hydroxide solution, and the alkali is then admitted into the chamber. When all the alkali is in the chamber, 2 or 3 ml. of acidified water is poured into the cup, followed by about 0.5 ml. of mercury. The mercury is then run into the chamber, dislodging any of the alkali solution which may have adhered in the part of the chamber under cock *b*.

To mix the solutions in the chamber, and to insure absorption of the last traces of carbon dioxide, the mercury in the chamber is raised and lowered three times, each lowering bringing the surface of the solution in the chamber, not to its bottom, but only to a point a little below the 10-ml. mark, and each raising bringing the pressure up to about atmospheric.

The solution meniscus in the chamber is then brought to a point a little below the 10-ml. mark at which p_1 was read, and is allowed to stand there for one minute while the solution drains down from the walls above the mark. During this time the temperature in the water jacket of the chamber is read and the corresponding carbon factor ascertained. Then the meniscus is raised exactly to the 10-ml. mark and reading p_2 is made on the manometer. The pressure, P_{CO_2} , of carbon dioxide from the combustion is calculated as $P_{CO_2} = p_1 - p_2 - c$, where c is the value of $p_1 - p_2$ as obtained in a blank analysis.

The milligram of carbon in the sample are calculated by the factors as given in the table below, which may be corrected if necessary by a factor obtained from control analyses of a standard pure substance.

$$\text{Milligrams carbon} = P_{CO_2} \times \text{factor}$$

FACTORS FOR CARBON CALCULATION

| Temperature ° C. | Factors ($a = 10.00$; $s = 3.00$; $i = 1.007$) |
|---------------------|---|
| 20 | 0.006954 |
| 21 | 922 |
| 22 | 890 |
| 23 | 859 |
| 24 | 828 |
| 25 | 798 |
| 26 | 769 |
| 27 | 740 |
| 28 | 711 |
| 29 | 683 |
| 30 | 655 |

To clean the chamber for the next analysis the used alkaline lactate solution is ejected and the chamber is washed once with dilute acid and

once with water. A rapid and convenient technic is the following: The mercury leveling bulb is lowered about 80 cm. below chamber *C* (Fig. 55, I) so that all mercury will drain out of the chamber. While it is draining, a few drops of the 2 *N* lactic acid are placed in the cup at the top of the chamber, together with enough water to fill the cup. The acidified water (but no air) is now let into the evacuated chamber. The leveling bulb is then raised and the solution expelled from the chamber. The washing is then repeated in the same manner, except that only distilled water is used. After the water is ejected, the mercury is lowered once more to the bottom of the chamber, and is allowed to rise rather slowly, so that the film of water adherent on the sides of the chamber is detached and floats up on the mercury. The drop of water thus collected, together with about 1 ml. of mercury, is run up into the cup, and the apparatus is ready for the next combustion.

SEMI-MICRO DRY COMBUSTION METHODS

Semi-micro dry combustion methods are usually compromises between the classical Liebig macro combustion method and the Pregl micro combustion method, approximately 200 mg. of sample being used in the former and about 4 mg. in the latter. In order to incorporate the obvious advantages of the micro method in regard to sample size and speed of analysis into combustion procedures, meso- and semi-macro, meso- and semi-micro combustion procedures have been devised.^{11-14, 17, 21, 25, 30, 33, 43, 46, 54, 70, 71, 87, 99-101, 116, 129, 130, 140, 148}

The necessity of using a microanalytical balance has been felt to be a distinct drawback in micro combustion work. Consequently J. B. Niederl and co-workers⁹⁶ investigated possible replacement of the microanalytical balance by an ordinary analytical balance in such combustion analyses. It was found that, with the apparatus described in this manual, samples of 1 to 15 mg. in weight can be analyzed *without* any changes in the apparatus or procedure, except that the sweeping-out process of the combustion gases has to be proportioned to the amount of sample used (100 ml. for milligram samples and 150 ml. for decamilligram samples). Merely the size of the sample needs to be enlarged in proportion with the precision of the ordinary analytical balance used; this corresponds approximately to 1 mg. of sample for each precision microgram of the balance. Incidentally, the early combustion analyses of F. Pregl^{106c} in 1911 and subsequently by L. E. Wise¹⁴⁶ in 1917 had been carried out in much the same manner.

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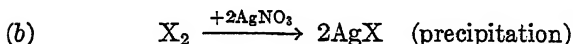
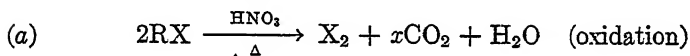
VI. DETERMINATION OF HALOGEN

GRAVIMETRIC METHODS

WET COMBUSTION (CARIUS) METHOD

Principle

The organic substance containing halogen is oxidized in a sealed tube ^{24, 39, 50, 71, 74, 80a, 87} in the presence of nitric acid at a temperature of 280–300° C., whereby the halogen is converted quantitatively into ionizable halogen which is precipitated and determined gravimetrically as silver halide.



Apparatus

Furnace (Fig. 36). The pressure tubes can be heated in any suitably constructed furnace; the one usually employed is a hollow round retort of heavy metal plate supported by a metal stand about 35 cm. high and 28 cm. long and covered at the top and sides with heavy asbestos or Transite plates. The retort has three or more apertures of approximately 1.5-cm. diameter and is heated by a suitable long burner. Electrically heated furnaces may even be provided with clock mechanisms between the relay and the furnace which automatically control the time of heating.

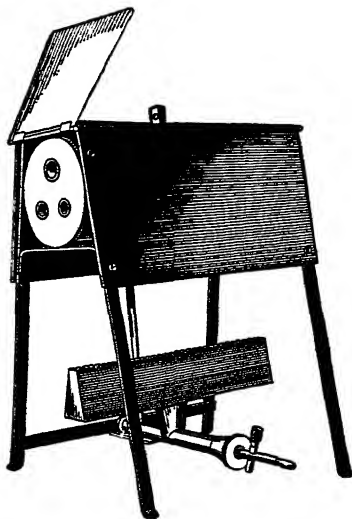


FIG. 36. Furnace.

Pressure Tubes. The pressure tubes are of straight-walled Pyrex glass without a constricted end. They are 20 cm. long, 9 to 10 mm. in

inside diameter, and should have a minimum wall thickness of 1 mm. and a round bottom. Tubes which possess a visible seam are unsatisfactory.

Filter Tubes (Fig. 37).^{80a, 87} Two types of filter tubes are available for the filtration of the silver halide. A filter of either type is 15 cm.



long and possesses a bulb 4 cm. long and 12 mm. wide and a stem 10 cm. long and of 4-mm. outer and 2.5-mm. inner diameter. The first type (a) contains an asbestos filter mat in the bulb-shaped portion over a constriction of 0.3-mm. diameter. The newer type (b) is supplied with a plate of sintered glass of medium density. To prepare a filter mat of the proper density the asbestos is deposited as follows: The filter tube is placed on the filtration apparatus and a 2-mm. layer of medium-fine Gooch crucible asbestos is filtered on top of the constriction and evenly pressed together with a sharp-edged glass rod; this is followed by a thin layer of fine asbestos and the whole is again pressed together to a mat of 2-mm. total thickness. The asbestos mat is washed first with about 250 ml. of distilled water, several times with hot cleaning solution, and again with distilled water and alcohol. Its orifice is then closed with a dust filter and the tube is dried with slight suction in the drying block at about 120° C. The filter tube is counterpoised with a ground-glass stoppered tare bottle and lead shot.

a

b

FIG. 37. a, Filter Tube with Asbestos Mat; b, Filter Tube with Sintered-Glass Plate.

The tube with the sintered glass filter plate (b) is preferable because it is easier to clean and the weight seems to show greater constancy. A filter plate of No. 3 porosity will retain the silver halide. However, these filters do not have a uniform porosity, and filters of the same density

(No. 3) usually show a rather wide variation in filter speed. Each filter tube should therefore be tested for its speed of filtration as follows: when the filter tube is placed on the filtration apparatus and attached to a good water pump, operating at maximum pressure, it should filter water at a rate of 70 ml. per minute.

The retentivity of a filter tube is checked by filtering a known amount of silver bromide, prepared by precipitating a weighed sample of potassium bromide (approximately 5 mg.), dissolved in 5 ml. of halogen-free

distilled water, with 2 ml. of a 5% silver nitrate solution in the presence of 1 ml. of concentrated nitric acid. The precipitated silver bromide is coagulated by heating on a steam bath for several minutes and is then filtered. The filter tube is rinsed, dried, and weighed as usual. Then 50 ml. of water is siphoned through the filter tube, after which the filter is again dried and weighed as before. A satisfactory filter tube should retain the precipitate to within 3 to 5 parts per 1000.

A new fritted glass filter, as well as a used one in which the pores have become clogged, is cleaned by boiling it for 15 minutes in dilute nitric acid

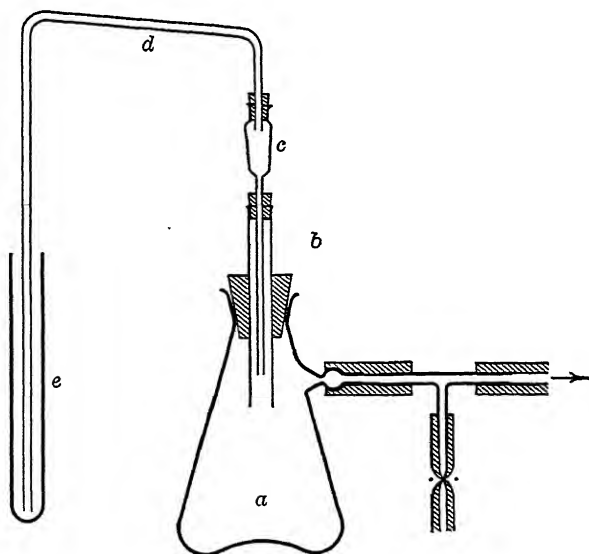


FIG. 38. Filtration Apparatus. *a*, Suction Flask; *b*, Adapter; *c*, Filter Tube; *d*, Siphon; *e*, Pressure Tube.

(1 : 1), then for the same time in distilled water, and rinsing it repeatedly, five or six times, with distilled water, and with alcohol. After the filter tube has been dried and weighed the procedure of rinsing it several times with distilled water and alcohol is repeated, and the tube is dried and weighed again; the two weighings should agree with each other within ± 10 micrograms. The above treatment with dilute nitric acid is important for the achievement of constancy of weight of the filter tube. Difficulty has been experienced in weighing fritted glass filter tubes to constant weight which previously had been cleaned with sulfuric acid-dichromate cleaning mixture. Upon subsequent treatment with nitric acid the same filter tubes became constant in weight.

Filtration Apparatus (Fig. 38). The apparatus consists of a 500-ml. suction flask provided with a tight-fitting rubber stopper, through which is inserted a glass adapter 8 cm. long and 8 mm. in diameter. This adapter is so adjusted that it extends several centimeters above the rubber stopper of the suction flask; its upper opening is provided with a perforated rubber stopper through which the filter is inserted during the filtration. Attached to the side arm of the suction flask is a T-tube carrying a screw clamp for the regulation of pressure.

The solution and the precipitate are siphoned from the pressure tube with the aid of a siphon, which is a glass tube of 2-mm. inner diameter, bent as shown in the illustration. The long vertical arm is 25 cm. long and is bent at an angle of about 80 degrees; then the siphon extends for a length of approximately 10 cm., where it is bent at an angle of about 100 degrees, so that the short arm, which is 6 cm. long, is parallel to the other.

Wash Bottles of the type shown in Fig. 6 are used as containers for the wash liquids such as distilled water and alcohol.

Reagents

All initial oxidizing and precipitating agents, as well as the wash liquids employed, must be free of halogen. The nitric acid, ethyl alcohol, and distilled water are tested for halogen by adding 5 drops of concentrated nitric acid and the same volume of silver nitrate solution to 5 ml. of the reagent and heating it on the steam bath for ten minutes. The reagent is considered halogen-free if, after the above treatment, no precipitation or even opalescence is discernible.

Concentrated Nitric Acid (sp. gr.: 1.42). It is redistilled in an all-glass apparatus over silver nitrate in vacuum.

Silver Nitrate. C.P. crystals.

Potassium Iodide Solution (30%). Thirty grams of c.p. potassium iodide is dissolved in enough distilled water to bring the total volume to 100 ml. The solution must be repeatedly filtered to ensure complete freedom from any suspended foreign matter such as dust particles. The solution is kept in a brown glass-stoppered bottle.

Ethyl Alcohol (95%). Redistilled over silver nitrate.

Distilled Water. Redistilled over silver nitrate.

Procedure

Preparation and Weighing of the Sample. A 5-mg. sample is usually taken for the chlorine, 7-mg. for the bromine, and 10-mg. for the iodine determination. With an ordinary analytical balance of proper sen-

sitivity and precision, about twice the above amounts of sample are taken, but at least 20 mg. for the iodine determination.⁷⁵ The amount of silver halide formed often weighs less than the original substance; the amount of substance used for the analysis may then exceed the above limits.

Filling the Pressure Tube. The sample is introduced into the pressure tube in the usual manner, that is, dry solids are introduced with the weighing tube (p. 44), low-boiling liquids (up to 200° C.) by means of a weighing pipet (p. 46), high-boiling liquids (above 200° C.) and semi-solids by employing capillaries which are open at both ends (p. 45). Then a crystal of silver nitrate, not more than a 10% excess over the required amount (about 10 mg. for chlorine and 15 mg. for bromine and iodine), is dropped into the pressure tube. After the silver nitrate, 0.3 ml. (5 or 6 drops) of concentrated nitric acid is added with a dropping pipet in such a manner that it rinses the lower half of the wall of the pressure tube, but wetting of the upper section, which is to be sealed off, is avoided.

If the substance is volatile, or if the halogen in the substance is so reactive that decomposition ensues at room temperature upon contact with the nitric acid, the substance should be introduced into the pressure tube in either a capillary or capillary pipet in such a manner that the substance is *above* the nitric acid until the pressure tube has been sealed. This is most easily accomplished by moistening the wall of the pressure tube, or the outside of the capillary containing the substance, with a drop of nitric acid and thus causing the capillary to adhere to the wall of the pressure tube. By means of a glass rod the capillary is pushed down to within several millimeters of the nitric acid already present in the pressure tube. For reactive solids, capillaries open at both ends, with the substance placed in the center, are used. After the pressure tube has been sealed the substance is brought in contact with the oxidizing agent through proper tilting of the pressure tube.

SEALING THE PRESSURE TUBE

The tube may be sealed either with an ordinary Tirrill gas burner or with a blast lamp.

*Sealing with the Tirrill Burner.*¹⁰² The pressure tube is held in both hands in a slightly inclined position and is preheated with a luminous flame, while it is constantly rotated, until deposits of carbon are obtained at the part of the tube where it is to be sealed off, that is, about 6 cm. from the open end. Then this area (Fig. 39a) is heated with a strong hissing flame, while the tube is slowly rotated. When the glass has

softened sufficiently so that the wall of the pressure tube begins to collapse, it is removed from the flame and, while still being turned, drawn out until it forms a constricted region about 2 cm. long (b). Then the flame is applied to the base of the constriction and the heating continued, while the tube is turned, until its wall collapses. After the wall of the pressure tube has thickened to form a solid glass rod, the tube is removed from the flame and drawn out as shown in (c). It

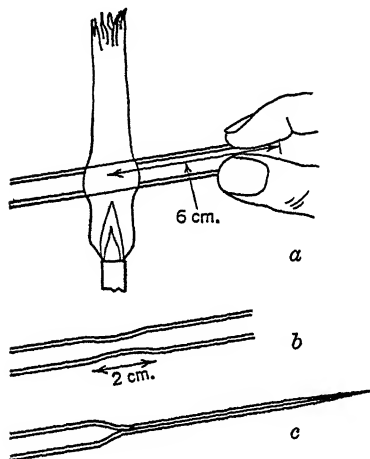


FIG. 39. Sealing of the Pressure Tube with a Tirrill Burner.

is sealed at the top to a point (d) by holding its tip in the outer cone of the flame, and then it is annealed in the luminous flame of the burner.

Sealing with the Blast Lamp. In sealing the pressure tube with the blast lamp it is advisable to fuse on a short piece of the same kind of tubing, which is made to serve as a handle. The pressure tube is heated over an area of 3 cm. at a point about 6 cm. from the junction, first with a luminous flame and then with a strong hissing flame, while it is constantly rotated, but without pulling, until its wall thickens to a capillary. Then the tube is removed from the flame and drawn out; the extended capillary is heated again with a small but strong flame at its base until the capillary collapses to form a solid

glass rod. This end is drawn out once more and after being cut with the flame it is fire-polished; the formation of a curved tip should be avoided.

Digestion. The sealed, but already cool, pressure tube is placed in the furnace and heated for one hour between 280 and 300° C., which is usually sufficient for most halogen compounds.

Opening of the Pressure Tube. At the end of the digestion period the tube is allowed to cool to room temperature in the furnace and then is pushed out with a glass rod, so that the sealed tip protrudes about 1 cm. beyond the end of the furnace. The tip is cautiously heated by passing over it the luminous flame of a Tirrill burner until any liquid caught in the tip is driven down into the tube. Next, the tip is heated directly below the point of taper with a small flame until the glass softens sufficiently to permit the internal pressure of the tube to blow

it open (Fig. 40a, b). After release of the pressure, a groove is filed around the tube with a sharp triangle file, or cut with a small Griffin glass-cutting wheel, somewhat below the point of taper. The area of the groove is moistened with water and then, with the tube held in an inclined position, the molten tip of a thin glass rod is pressed against the groove; this procedure is repeated if necessary until a crack encircles the tube. The pressure tube, while held in a towel, is pulled apart and the edge fire-polished. If it is pulled apart rather than broken by exerting angular force, glass splinters will rarely enter the tube.

Filtering the Precipitate. The clean filter tube is inserted in the adapter, and the short arm of the siphon, which is provided with a smooth rubber stopper, is placed on the filter tube. The contents of the pressure tube are diluted with 2 to 3 ml. of halogen-free distilled

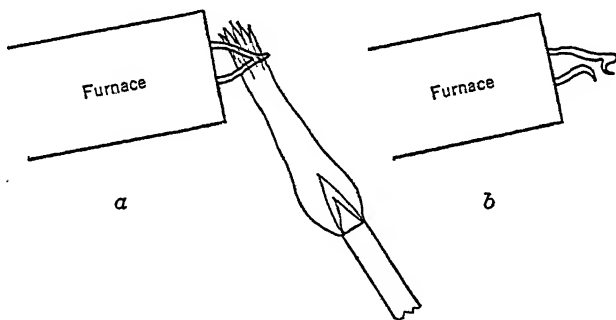


FIG. 40. Releasing the Pressure.

water, or with no more than enough to fill two-thirds of the tube; the tube is placed in a 250-ml. beaker half filled with water which is then boiled for several minutes. The hot water in the beaker is replaced by cold water and the pressure tube is placed in it to cool. When cool, the pressure tube is placed under the siphon of the filtration apparatus. The precipitate is stirred with the long arm of the siphon and lumps of the precipitate may be crushed at the same time. Suction is then applied and the precipitate and wash liquid are siphoned over, but the speed of filtration is so regulated with a screw clamp on the vertical arm of the T-tube between the pressure tubing and the suction flask that the liquid drops on the filter mat, or sintered glass plate, at a rate of 1 to 2 drops per second. The bulb of the filter tube should never be filled completely during the filtration; before this occurs the long arm of the siphon is raised above the meniscus of the liquid in the pressure tube to allow the liquid in the bulb of the filter tube to be drawn off.

After the liquid and whatever precipitate was carried over have been siphoned off, the suction is broken by opening the screw clamp; then the tube is filled two-thirds full with distilled water by spraying the wash liquid over the inner wall of the pressure tube while it is being rotated. Suction is again applied and the liquid drawn off; at this point of the procedure it is advisable to admit air bubbles into the siphon by repeatedly raising the siphon above the liquid in the pressure tube, because these air bubbles act as a scrubber and very effectively remove particles of precipitate lodged in the horizontal section of the siphon. This rinsing is repeated with alcohol, then with distilled water, and once more with alcohol; particles of precipitate clinging to the wall of the pressure tube are scraped off with the siphon tube.

After this procedure of rinsing the siphon is removed from the filter tube, but the stopper as well as the short part of the siphon protruding from the stopper are rinsed with alcohol, which is collected in the filter tube and filtered. The suction is then broken and the filter tube is filled to the rim with distilled water which is drawn off; this rinsing is repeated twice with alcohol. After the procedure of rinsing, the filter tube is removed from the filtration apparatus, its outside is wiped dry with a towel, and its orifice is closed with a dust filter; next, the filter tube is connected to a suction pump with a flexible rubber tubing which is intersected by a T-tube for the purpose of regulating the pressure as well as for breaking the suction.

The filter tube is dried by placing the bulb-shaped part in the wide groove of the heating block which previously has been heated to between 110 and 115° C. Barely perceptible suction is applied; after five minutes the shaft of the filter tube is placed in the narrow groove and moved up after two or three minutes to dry the remaining portion of the stem. Then the filter tube is removed from the drying block, laid on the table, and allowed to cool under suction for five minutes, after which the suction is gradually broken by opening the screw clamp on the T-tube. Finally, while being held in a vertical position, the filter tube is wiped once with a moist flannel and three times with a dry chamois. After wiping, the filter tube is placed on a metal rack and left near the balance for fifteen minutes before it is weighed within ± 10 micrograms if a microanalytical balance is used, and within ± 1 deflection unit if an ordinary analytical balance is employed. The zero reading of the balance must also be determined and should be taken during the fifteen minutes preceding the weighing of the filter tube.

Dissolving the Precipitate. After the filter tube has been weighed it is placed on the filtration apparatus and the bulb is filled with 30% potassium iodide solution with the aid of a medicine dropper; this solu-

tion is allowed to run off slowly by itself, or if this is too slow, that is, less than 1 drop per second, under gentle suction. This process is repeated with another portion of the same solution, and if the precipitate has not dissolved by this time the treatment is repeated. Particles of glass should not be mistaken for undissolved silver halide. Finally, the filter tube is washed twice again, but more rapidly, with potassium iodide solution, five times with distilled water, and twice with alcohol. Then it is dried, allowed to cool, wiped, and weighed as before; the difference in weight between the first and second weighings represents the weight of the silver halide obtained.

The above procedure of weighing the filter tube after the filtration of the precipitate, then dissolving the precipitate, and weighing back the filter tube is recommended for students learning the technic of the determination, or if glass splinters have contaminated the precipitate, or when substances are analyzed which required the use of weighing pipets or capillaries; it, therefore, represents a procedure fulfilling all requirements. If, however, substances are analyzed which can be weighed with the weighing tube and the precipitate was not contaminated with glass splinters when the pressure tube was opened, then a somewhat more rapid procedure of weighing can be adopted. In this procedure the filter tube is washed, dried, and weighed while the substance is digested in the furnace, and the weight of the filter tube with the precipitate is the final weight of the first determination; then, without dissolving the precipitate, the next filtration is carried out, and thus the difference between the last two weighings represents the weight of the precipitate of the second determination. This may be continued until an entire series of analyses has been made, thereby effecting the saving of one weighing between each of two analyses. It is advisable, however, to start with a clean filter and to dissolve the precipitate after finishing a series of determinations.

| Time: | Minutes |
|---|---------|
| Weighing of the sample..... | 10 |
| Preparation, filling and sealing of the pressure tube. . . | 15 |
| Digestion..... | 60 |
| Filtration..... | 15 |
| Drying of the filter tube..... | 15 |
| Wiping and weighing of the filter tube with the precipitate | 20 |
| Dissolving the precipitate..... | 10 |
| Drying of the filter tube..... | 15 |
| Wiping and reweighing the filter tube..... | 20 |
| Total..... | 180 |

Calculation:

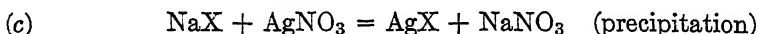
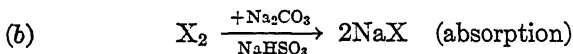
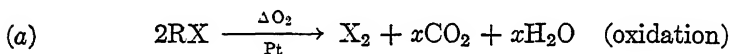
Log of weight of silver halide,
 Plus log of the respective factor,
 Plus negative log of weight of sample;
 Antilog of total = percentage halogen.

Factors:

Chlorine as silver chloride: 0.2474; log, 39340.
 Bromine as silver bromide: 0.4255; log, 62894.
 Iodine as silver iodide: 0.5405; log, 73284.

DRY COMBUSTION METHOD**Principle**

The substance is combusted in a suitably constructed combustion tube in the presence of oxygen, and the decomposition products are passed over heated platinum contacts to ensure complete oxidation.^{31, 50, 71, 80a, 87} The halogen is absorbed in a solution of sodium carbonate containing sodium bisulfite to reduce any chlorate, bromate, or iodate. The absorption reagent which is distributed over the spiral of the combustion tube is transferred to a test tube, and the halogen is precipitated as silver halide by the addition of silver nitrate solution and concentrated nitric acid. The precipitated silver halide is transferred to a filter tube and weighed.

**Apparatus***Oxygen Tank and Gas Wash Bottle.*

Combustion-Spiral Tube (Fig. 41). This tube is made of quartz, Pyrex glass No. 172, or Supremax glass, and is about 64 cm. long and 8 mm. in inner diameter. One end of the tube is drawn out to a capillary of approximately 0.3-mm. inner and 5-mm. outer diameter. A spiral of Pyrex glass approximately 20 cm. long is placed against this capillary and held in position by an indentation in the combustion tube. The mouth of the combustion tube is provided with a perforated rubber stopper in which a capillary is inserted.

Combustion Stand. This is of the same type as that illustrated in Fig. 21.

Platinum Contacts. These are 5 cm. long and 7.5 mm. in diameter, or just somewhat smaller than the bore of the combustion tube. The

contacts may vary in form, but those having a starlike cross section are preferable. The ends of the contacts are provided with loops of platinum wire. They are cleaned by boiling in dilute nitric acid and heating in a non-luminous flame; to protect the contacts from dust they are kept in a covered Petri dish.



FIG. 41. Halogen Combustion Tube. *a*, Spiral; *b*₁ and *b*₂, Platinum Contacts; *c*, Platinum Boat.

Precipitation Tubes. Test tubes of Pyrex glass of 4.5-cm. inner diameter and 20-cm. length are used for the transfer and precipitation of the halogen.

Filter Tubes, Filtration Apparatus, and Wash Bottles. These devices are the same as those used for the wet combustion method (pp. 152-154).

Reagents

All reagents must be halogen-free (see p. 154).

Concentrated Nitric Acid. This is distilled over silver nitrate in vacuum.

Sodium Carbonate Solution. Twenty-five grams of halogen-free sodium carbonate is dissolved in 100 ml. of boiling, halogen-free distilled water. The warm solution is poured into a reagent bottle provided with a rubber stopper and covered with a small beaker.

Perhydrol. Completely halogen-free.

Silver Nitrate Solution (5%). Five grams of c.p. silver nitrate is dissolved in 100 ml. of halogen-free distilled water to which a few drops of nitric acid have been added. It is stored in a brown reagent bottle.

Sodium Bisulfite Solution. This solution is prepared from the halogen-free saturated sodium carbonate solution by slowly introducing halogen-free sulfur dioxide with cooling, because otherwise appreciable quantities of thiosulfate are formed which cause the separation of sulfur on acidification. The sulfur dioxide is generated in a small generator by slowly adding concentrated sulfuric acid to sodium bisulfite and passing the liberated sulfur dioxide through a tube containing glass wool, which is moistened with halogen-free saturated sodium carbonate solution, before it is passed into the cooled sodium carbonate solution. The sodium bisulfite solution so obtained is stored in ampules of approximately 25-ml. capacity drawn out to a long capillary. Before use the capillary is opened near its top and the solution expelled from the ampule drop by drop; then the capillary is sealed off again.

This solution should conform to the following test: Twenty milliliters, made alkaline with halogen-free sodium carbonate solution to

which 3 or 4 drops of perhydrol have been added, is warmed on a steam bath for five minutes. After cooling, a mixture of 1 to 2 ml. of halogen-free nitric acid and 0.5 ml. of 5% silver nitrate solution is added. The reaction mixture is then heated for an additional ten minutes on a steam bath, and the solution can be considered free from halogen when no precipitation or turbidity occurs.

Ethyl Alcohol (95%).

Distilled Water.

Procedure

Preparation and Filling of the Combustion Tube. Before every determination the combustion tube must be cleaned with hot cleaning solution which is siphoned up through the capillary end and allowed to remain in the tube for ten minutes. Then the cleaning solution is drained off and the combustion tube is washed successively with tap water, distilled water, and alcohol; after closing the mouth of the tube with a dust filter, the tube is dried on the suction pump with moderate heating. When it has cooled to room temperature, 2 ml. of sodium carbonate solution is mixed with 2 drops of sodium bisulfite solution in a wide test tube and this mixture is siphoned up to the indentation, *but not beyond*, so that the entire spiral is well moistened with the absorption liquid. To prevent saliva from entering the combustion tube in siphoning up the absorption liquid, the mouth of the tube is protected by a dust filter; in all subsequent operations which require siphoning up or expelling of liquid the same precautionary measure is employed. After the spiral has been well moistened with the absorption liquid by rotating the combustion tube, the excess liquid is permitted to drain off and is discarded. The test tube which contained the absorption liquid is placed over the capillary end of the combustion tube where, adequately supported, it remains during the entire combustion. Next, the freshly cleaned platinum contacts are introduced; the first is placed about 8 cm. from the indentation and the second about 5 cm. from the first. The mouth of the combustion tube is closed with a small cotton plug, and the long wire gauze is pushed to within 5 cm. of the indentation, but still should cover completely the area occupied by the platinum contacts. The short wire gauze is placed over the front part of the combustion tube; the cotton plug is removed and replaced by the rubber stopper with the capillary connection.

Combustion. The oxygen necessary for the combustion is obtained from a tank and then passed through a gas wash bottle containing a saturated solution of sodium carbonate. The oxygen enters the combustion tube through the capillary tube at a rate of 5 to 6 ml. per minute, a rate which is determined by counting the number of bubbles

rising in the wash bottle.* Next, the long burner under the long wire gauze of the combustion tube is lighted and the platinum contacts heated to a dull red. It is important that the platinum contacts be heated to redness before the sample is introduced into the combustion tube, because otherwise volatile substances may vaporize and pass through the system without being completely oxidized.

The size of the sample is chosen according to the percentage and kind of halogen present in the compound and whether a microanalytical or ordinary analytical balance is used. The substance is weighed in a platinum boat which is then placed within 7 cm. of the platinum contact. The short wire gauze is moved 5 cm. in front of the platinum boat, and the combustion is carried out by gradually advancing a gas burner toward the substance, heating directly under it for ten minutes, and then moving the flame up to the long burner. The entire combustion requires approximately thirty minutes. The combustion may be slowed down when volatile substances are combusted, in order to ensure sufficient contact of the combustion products with the platinum catalysts. After the completion of the combustion both burners are extinguished and the combustion tube is permitted to cool to room temperature in an atmosphere of oxygen. Then the wire gauzes, the platinum boat, and the two platinum contacts are removed. The upper part of the combustion tube is wiped with a clean towel and then is clamped vertically to a stand, without being removed from the wide test tube with which it was covered during the combustion.

Precipitation and Filtration. Eight milliliters of distilled water is poured into the precipitation tube (receiver *A*), 3 or 4 drops of sodium bisulfite solution is added, and the mixture is aspirated into the combustion tube which is protected with a dust filter. The wash liquid should cover the spiral completely and extend 1 cm. beyond the indentation. Then the dust filter is removed, the mouth of the combustion tube closed with the index finger, the tube transferred to a second precipitation tube (receiver *B*), and the wash water is permitted to drain off. Receiver *A* is rinsed with 8 ml. of distilled water which is aspirated into the combustion tube and drained into receiver *B* as before. This procedure is repeated a third time with the same amount of distilled water; in this manner the quantitative transfer of the absorption liquid from

* The velocity of the oxygen is determined by connecting the wash bottle to a Mariotte flask and measuring the volume of water displaced in thirty seconds. To obtain the correct volume of oxygen in subsequent determinations, the number of bubbles rising during this interval is counted and then the needle valve of the oxygen tank is simply adjusted to give again the required number of bubbles. It is necessary to make sure that the gas wash bottle is leak-proof, because otherwise the calibration by counting the bubbles is of no value.

the combustion tube to receiver *B* is accomplished. Finally, the inside and the capillary tip of the combustion tube are rinsed with a small amount of distilled water which is also collected in receiver *B*. Two drops of perhydrol are added to the solution in receiver *B* to oxidize any excess of bisulfite, and then the contents of receiver *B* are heated on the steam bath for three to five minutes. After this, 1 ml. of concentrated nitric acid and 2 ml. of 5% silver nitrate solution are added to the contents in the receiver; the receiver is covered with an evaporating dish and heated on the steam bath for fifteen minutes. To facilitate the coagulation of the precipitated silver halide, the receiver is taken from the steam bath at about two-minute intervals and shaken. Finally, the receiver is placed in a beaker of cold water, and, as soon as the supernatant liquid is perfectly clear, the precipitate is ready to be filtered as described on p. 157. Since in this determination no glass splinters can be present in the precipitate, the more rapid procedure of weighing the precipitate (see p. 159) can be employed.

Iodine. The determination of iodine by this method requires a slightly modified procedure. A larger sample, about 10 mg., or twice as much if weighed on an ordinary analytical balance, is taken and the combustion is modified to the extent that iodine remaining as a sublimate in front of the spiral must be driven into the absorption liquid by cautiously heating this part of the combustion tube. The transfer of the absorption liquid is carried out as described above, except that 2 drops of sodium bisulfite solution are also added to the 8 ml. of distilled water used for the second washing of the combustion tube and 4 or 5 drops of perhydrol is added to the combined wash water, because of the greater amount of sodium bisulfite solution used. The combined extracts and washings, however, are not heated, but allowed to stand at room temperature for ten minutes. Then 1 ml. of concentrated nitric acid and 2 ml. of 5% silver nitrate solution are added, and the precipitation and filtration are carried out as described above.

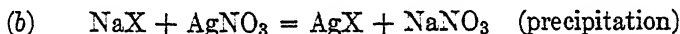
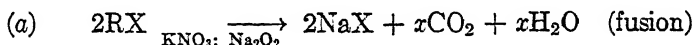
| Time: | Minutes |
|--|---------|
| Weighing of the sample..... | 10 |
| Preparing and filling of the combustion tube..... | 25 |
| Combustion..... | 30 |
| Cooling of the combustion tube (during this period and during the latter part of the combustion the filter tube may be weighed)..... | 20 |
| Filtration..... | 15 |
| Drying of the filter tube..... | 15 |
| Wiping and weighing of the filter tube with the precipitate..... | 20 |
| Total..... | 135 |

Calculation:

Log of weight of silver halide,
 Plus log of the respective factor (p. 297),
 Plus negative log of weight of sample;
 Antilog of total = percentage of halogen.

FUSION METHOD*BOMB METHOD***Principle**

The organic halogen compound is fused with a mixture of potassium nitrate, sodium peroxide, and cane sugar in a microbomb^{37, 38} to yield ionizable halogen which is precipitated and weighed as silver halide.

**Apparatus**

Bomb (Fig. 42). The bomb employed for the fusion consists of a fusion cup, 2.5 cm. deep and 1.3 cm. in inside diameter; it is made of illium (nickel-chromium alloy). Its wall is 1.5 mm. thick, and it has a lip 3 mm. wide, on which the lid and the lead washer rest. The cup has a rounded base and a small eyelet at the bottom. The lid of the bomb is held securely in position by an arched clamp with a tight-fitting screw.

Precipitation Tubes, Filter Tube, Filtration Apparatus, and Wash Bottles. These are the same as mentioned under 'Dry Combustion Method' (p. 161).

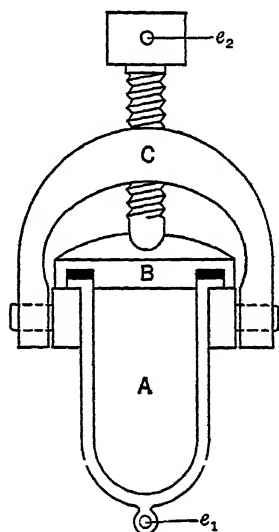


FIG. 42. Bomb; A, Cup; B, Lid; C, Screw Clamp; e_1 and e_2 , Eyelets.

Reagents

All reagents must be halogen-free and correspond to the test for the absence of halogen as described on p. 154.

Potassium Nitrate. C.P. crystals.

Sodium Peroxide. C.P.

Concentrated Nitric Acid (sp. gr.: 1.42).

Dilute Nitric Acid (0.1%).

Silver Nitrate Solution (5%).

Hydrazine Sulfate. C.P.

Cane-Sugar, C.P., or *d-Glucose*, C.P.

Ethyl Alcohol (95%).

Distilled Water.

Procedure

Mixing. Three hundred milligrams of a mixture of potassium nitrate and sugar in the proportion of 3 : 1 and 1.5 grams of sodium peroxide are mixed in a glass-stoppered weighing bottle. One-third of this mixture is placed in the cup of the bomb, and an appropriate amount of the substance to be analyzed is added. Then the rest of the mixture is added, the lid of the bomb is screwed tight, and the contents are thoroughly mixed by shaking the bomb. To facilitate complete oxidation, efficient mixing is important. After the bomb has been tapped repeatedly so that its contents settle to the bottom, the reaction mixture is ready for the fusion.

Fusion. The bomb is held by the head of the screw clamp either with tongs or by a piece of stout wire passed through the eyelet in the head of the screw and then it is gradually lowered about one-third into the upper part of a small but non-luminous flame of a gas burner; care should be taken to avoid heating too near the lid. The fusion is complete in about ten seconds; the actual fusion can be determined readily because the resulting disturbance within the bomb can be felt. Theoretically the fusion is then completed, but it is advisable to hold the bomb in the flame for an additional five seconds in order to fuse the entire reaction mixture thoroughly. Then the bomb is cooled under the tap.

Precipitation and Filtration. The bomb is first rinsed on the outside with distilled water, then opened, and the inside of the lid is washed with hot distilled water; the washings are collected in a precipitation tube. Next, the cup is placed in the precipitation tube and enough hot distilled water is added to cover the bomb, which is agitated to effect complete solution of the fusion mixture. After the fusion mixture

has completely dissolved, the cup is lifted up with a heavy platinum wire and thoroughly rinsed with hot distilled water. Then the cup is picked up with platinum-tipped forceps at the eyelet and the inside of the cup is also washed with hot distilled water, which is added to the original solution.

Chlorine. This solution is cooled in an ice bath and acidified with concentrated nitric acid. The acidified solution is filtered into another precipitation tube, and the filtrate is treated with 1 ml. of 5% silver nitrate solution; it is reheated on a steam bath and the precipitate is filtered as described on p. 157.

Bromine and Iodine. The combined extracts and washings are neutralized to a slight pink with nitric acid, phenolphthalein being used as the indicator. Then 100 mg. of hydrazine sulfate is added and the mixture is heated on a steam bath for fifteen minutes. After the mixture has been filtered into another precipitation tube, it is acidified with 0.5 ml. of concentrated nitric acid; 1 ml. of 5% silver nitrate solution is added; then it is reheated on the steam bath and the precipitate filtered as described on p. 157.

It is expedient to weigh the required quantities of fusion mixture and hydrazine sulfate and to place these reagents in a spoon of appropriate capacity, or in a small test tube, and mark the level of the reagents. Since the amount of reagent used need be only approximate, later quantities can be measured in this manner instead of being weighed.

Time:

| | <i>Minutes</i> |
|--|----------------|
| Weighing of the sample..... | 10 |
| Preparation and filling of the bomb..... | 10 |
| Fusion..... | 5 |
| Extraction and precipitation..... | 20 |
| Wiping and weighing of the filter tube..... | 20 |
| Filtration..... | 15 |
| Drying of the filter tube..... | 15 |
| Wiping and weighing of the filter tube with the precipitate..... | 20 |
| Total..... | 115 |

Calculation:

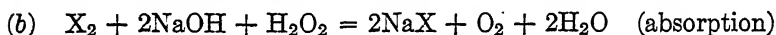
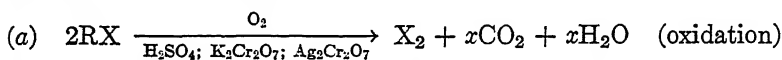
Log of weight of silver halide,
 Plus log of the respective factor (p. 297),
 Plus negative log of weight of sample;
 Antilog of total = percentage halogen.

TITRIMETRIC METHODS

CHLORINE AND BROMINE

Principle

The organic substance containing chlorine or bromine is placed in a reaction flask and decomposed with concentrated sulfuric acid in the presence of a mixture of potassium dichromate and silver dichromate at a temperature of 115 to 125° C.¹¹⁵ The combustion is carried out in oxygen, and the halogen is driven into a receiver filled with an excess of 0.01 *N* sodium hydroxide solution, to which 1 ml. of 30% hydrogen peroxide has been added.



The excess of 0.01 *N* sodium hydroxide is titrated with 0.01 *N* acid, and from the amount of alkali used the percentage of chlorine or bromine is calculated. The presence of iodine does not interfere, because it is oxidized to iodate; volatile substances, or substances containing as additional elements nitrogen or sulfur, however, cannot be analyzed by this method.

Apparatus

Oxygen Tank and Gas Wash Bottle. The same oxygen tank and wash bottle as described on p. 162 is used; the flow of oxygen, 8 ml. per minute, is standardized with the aid of a Mariotte flask.

Combustion Apparatus (Fig. 43). The apparatus, made of Pyrex glass, consists of the inlet tube (a), the dropping funnel (b), the introduction tube (c), the reaction flask (d), the delivery tube (e), the absorption buret (f), and the spiral (g). The dropping funnel has a capacity of about 5 ml.; it is 4 cm. long and 2 cm. in diameter. It ends in a stopcock, to which is sealed the introduction tube; this tube is 11 cm. long and has a 4-mm. outer and 2-mm. inner diameter. The reaction flask is 9.5 cm. long over all and has a heart-shaped bulb of 5-ml. capacity at the bottom. Its neck is 7.5 cm. long, 1.2 cm. in diameter, and ends in an interchangeable ground-glass joint. The delivery tube is sealed to the dropping funnel below the stopcock; it extends horizontally for 8 cm. and then descends vertically for 27 cm. The horizontal arm carries a split cylindrical cork for the attachment of the apparatus to a stand; a small glass knob is fused to the vertical arm of the delivery

tube 1 cm. above its tip to hold the spiral in place. The absorption buret is 30 cm. long over all and has a cylindrical funnel 6 cm. long and 3.5 cm. in diameter, which narrows down to a buret 17 cm. long and 1.3 cm. in diameter. A stopcock is sealed to the end of the buret at an oblique angle, and below the stopcock is an outlet tube of 4-cm. length and 1-mm. bore.

Heating Block. The apparatus is provided with either a heating block or a suitable metal or oil bath. The heating block consists of a piece of aluminum having a wide enough opening for the insertion of the reaction flask and a smaller one for the thermometer; it is heated by a microburner. The oil bath may be of any convenient shape and is also heated by a microburner.

Titration Equipment. Titration flasks, burets, steaming apparatus, as described under "Standard Solutions" (p. 51), are required.

Reagents

Concentrated Sulfuric Acid (sp. gr.: 1.84). This should be taken from a fresh bottle.

Potassium and Silver Dichromate.

This mixture consists of equal parts of potassium dichromate (c.p.) and silver dichromate. The silver dichromate is prepared⁵ by boiling 10 grams of silver nitrate and 6 grams of chromic acid in 1 liter of distilled water until the reagents have completely dissolved. The solution is filtered while still hot and is left standing over night. The silver dichromate which crystallizes out in brown crystals is filtered off on a Büchner funnel, washed repeat-

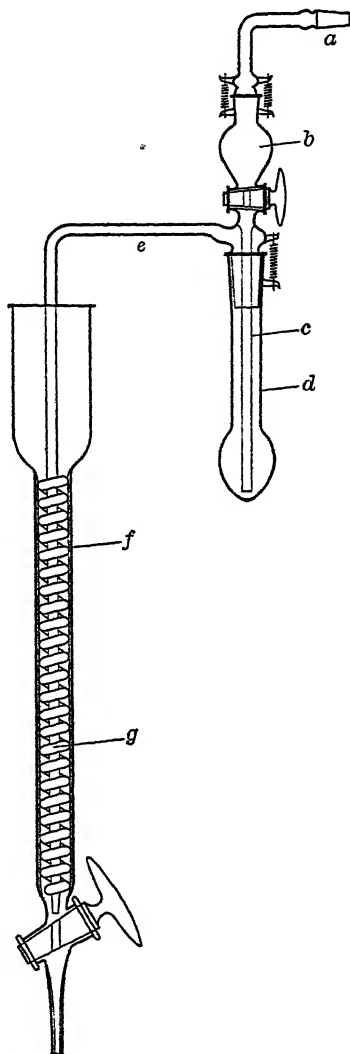


FIG. 43. Apparatus for the Alkali-metric Determination of Chlorine and Bromine. Explanation in Text.

edly with distilled water, and dried in the desiccator over phosphorus pentoxide. It is powdered, mixed with potassium dichromate, and stored in a brown ground-glass stoppered reagent bottle.

Perhydrol (30% hydrogen peroxide). Even the guaranteed acid-free perhydrol shows a slight acidic reaction, and consequently this acidity has to be determined for each fresh bottle. The 0.01 *N* sodium hydroxide solution used for the neutralization of 1 ml. of perhydrol, the *blank*, must be deducted from the total 0.01 *N* sodium hydroxide solution used for a regular determination. This titration is carried out by measuring 1 ml. of perhydrol with a delivery pipet into a 50-ml. Erlenmeyer flask, adding 5 ml. of distilled water, and boiling the solution for a few seconds. A trace of methyl red indicator solution is added and the solution titrated with 0.01 *N* sodium hydroxide solution to a canary-yellow coloration.

0.01 *N* Acid Solution.

0.01 *N* Sodium Hydroxide Solution.

Methyl Red Indicator Solution.

The preparation and standardization of the 0.01 *N* solutions, as well as the preparation of the methyl red indicator solution, are described under "Standard Solutions" on pp. 54-56.

Procedure

Preparation of the Apparatus. Before a series of analyses, especially after having been idle for some time, all parts of the apparatus are cleaned with warm cleaning solution; exhaustively rinsed with tap water, distilled water, and ethyl alcohol; and dried in the drying oven at 120° C. The stopcock of the absorption buret, which is removed during the cleaning of the apparatus, is sparingly but nevertheless sufficiently greased to make the barrel transparent. The perfectly dry apparatus, with the exception of the reaction flask and the absorption buret, is clamped to a stand, and the heating block or oil bath is heated to 115 to 125° C. A volume of 8 ml. of 0.01 *N* sodium hydroxide solution, accurately measured, is run from the microburet into a steamed-out 125-ml. Erlenmeyer flask, and 1 ml. of perhydrol is added to the alkali with a 1-ml. delivery pipet. This solution is poured into the absorption buret, which is then attached to the apparatus so that the tip of the delivery tube extends within 5 mm. of the stopcock; the buret is held in place with the aid of a loose clamp which allows free rotation of the buret. The Erlenmeyer flask is placed under the outlet tube of the stopcock, because it is used again to collect the absorption liquid after the combustion. The sample is weighed in the weighing tube or,

if a liquid, in the weighing capillary and transferred to a clean, dry reaction flask. About 0.5 gram of the dichromate mixture is added to the substance with a small spoon of known capacity, so that the amount of reagent, which need be only approximate, does not have to be weighed. Then the ground-glass joint of the reaction flask is lubricated with a few drops of sulfuric acid, after which it is attached to the apparatus and fastened with two wire springs. The stopcock of the dropping funnel is also lubricated with a little sulfuric acid and turned shut; 2 ml. of concentrated sulfuric acid is placed in the dropping funnel with a delivery pipet, and the inlet tube, which connects the apparatus to the oxygen tank, is inserted in the dropping funnel. Then the oxygen, which previously has been regulated to a velocity of 7 to 8 ml. per minute, is turned on and the stopcock gradually opened, the sulfuric acid being forced thereby slowly down into the reaction flask.

Heating and Titration. After the sulfuric acid has run into the reaction vessel and the initial reaction has subsided, as evidenced by a regular rise of bubbles from the delivery tube in the absorption buret, the heating block or oil bath is raised high enough to cover completely the bulb of the reaction flask, which is then heated to 115–125° C. for thirty minutes. At the end of this period the stopcock above the reaction flask is closed and the inlet tube disconnected from the dropping funnel; then the stopcock below the absorption buret is opened and the absorption liquid drained into the Erlenmeyer flask. The stopcock is again closed and the absorption buret rinsed, while being rotated, with 4 to 5 ml. of distilled water. Before the wash liquid is drained into the Erlenmeyer flask, the apparatus is again connected to the oxygen tank, the stopcock below the dropping funnel is opened, and oxygen is bubbled through the system for about twenty seconds to expel any absorption liquid remaining inside of the delivery tube. The rinsing of the absorption buret is repeated twice in precisely the same manner. A trace of methyl red indicator solution is added to the solution in the Erlenmeyer flask and the solution titrated with 0.01 *N* acid to a distinct red; then it is boiled for about twenty seconds to expel carbon dioxide. Another trace of indicator solution is added and the solution is titrated back with 0.01 *N* sodium hydroxide solution to a canary-yellow coloration. Should the solution turn yellow upon boiling, more acid is added and the boiling repeated.

The apparatus must be rinsed with distilled water and ethyl alcohol and dried before it is used for the next analysis. The substance is most conveniently weighed during the thirty minutes of the combustion, because the apparatus, aside from an occasional check of the temperature and velocity of the oxygen, needs no further supervision.

| Time: | Minutes |
|---|---------|
| Weighing of the sample..... | 10 |
| Preparation and filling of the apparatus..... | 20 |
| Combustion..... | 30 |
| Rinsing the absorption buret..... | 5 |
| Titration..... | 10 |
| Total..... | 75 |

Calculation:

Log of ml. 0.01 *N* sodium hydroxide solution,
 Plus log of atomic weight of the respective halogen,
 Plus negative log of weight of sample;
 Antilog of total = percentage halogen.

Factors:

Chlorine: 35,457; log, 54970.
 Bromine: 79,916; log, 90263.

IODINE**Principle**

The organic iodine compound is combusted catalytically in an atmosphere of oxygen ^{66, 108, 109} to yield iodine, carbon dioxide, and water. The iodine is absorbed in a suitable medium and is oxidized with bromine to form iodic acid which is determined iodometrically.

The steps involved are the following:

- (a) $2RI \xrightarrow[\text{Pt, O}_2]{\Delta} I_2 + xCO_2 + xH_2O$ (combustion)
- (b) $I_2 + Br_2 = 2IBr$
- (c) $IBr + 2Br_2 + 3H_2O = HIO_3 + 5HBr$
- (d) $HIO_3 + 5HI = 3I_2 + 3H_2O$
- (e) $3I_2 + 6Na_2S_2O_3 = 6NaI + 3Na_2S_4O_6$ (titration)

Apparatus

Oxygen Tank and Gas Wash Bottle.

Combustion Tube.

Combustion Stand.

Platinum Contacts.

Precipitation Tubes.

These five items are the same as described under "Dry Combustion Method" on p. 160.

Titration equipment is the same as described under "Standard Solutions" on p. 51.

Reagents

Sodium Hydroxide Solution (5%). Five grams of c.p. sodium hydroxide is dissolved in 100 ml. of distilled water.

Sodium Acetate Solution (20%). This is prepared by dissolving 20 grams of sodium acetate ($\text{CH}_3\text{COONa} + 3\text{H}_2\text{O}$) in 100 ml. of distilled water.

Solution of Sodium Acetate in Glacial Acetic Acid (10%). Ten grams of sodium acetate ($\text{CH}_3\text{COONa} + 3\text{H}_2\text{O}$) is dissolved in 100 grams of glacial acetic acid.

Bromine. Free from iodine; it is kept in a dropping bottle.

Formic Acid (80 to 100%). This is kept in a dropping bottle.

Potassium Iodide Solution (free from iodate). Ten per cent aqueous solution.

Sulfuric Acid (2 N).

0.01 N Sodium Thiosulfate Solution.

Starch Indicator Solution.

Methyl Red Indicator Solution.

The standard solutions and the indicator solutions are the same as described under "Standard Solutions" on pp. 53-57.

Distilled Water. It is advisable to redistil the distilled water which is used as wash liquid or for the preparation of the various reagents.

Procedure

Combustion. The spiral combustion tube is cleaned and dried as described on p. 162. For the absorption of iodine, 5 ml. of 5% sodium hydroxide solution is aspirated from a precipitation tube up to the end of the spiral; then the excess absorption liquid is permitted to drain back into the tube and is discarded. The empty tube is then placed over the outlet of the combustion tube. Next, the platinum contacts are inserted in the combustion tube, the pieces of wire gauze are placed over it, and the long burner is lighted. After the platinum contacts have been heated to a dull red, the substance, which is weighed in a platinum boat if a solid, or in a capillary if a liquid, is introduced, and finally the combustion tube is connected to the oxygen tank. The combustion is carried out as described on p. 162, except that the oxygen passing through the system is adjusted to a velocity of 3 ml. per minute. Caution must be exercised during the combustion so that no iodine sublimes behind the movable burner; should this occur, but provided that it is not too close to the rubber stopper, then the sublimate is

driven back toward the platinum contacts by appropriate heating. After completion of the combustion the section of the combustion tube between the long burner and the beginning of the spiral must be examined for deposits of iodine, which, if present, are driven into the absorption liquid by cautious heating with the gas burner. The combustion tube is permitted to cool while oxygen is passed through at the normal rate. During this period the necessary preparations for the titration are made.

Transfer and Titration. Measured with a delivery pipet, 5 ml. of 20% sodium acetate solution is placed in a 125-ml. Erlenmeyer flask (receiver *B*) having a ground-glass stopper. For the rinsing of the combustion tube 4 ml. of 10% sodium acetate solution in glacial acetic acid is placed in a test tube and 2 or 3 drops of bromine is added. Then the wire gauzes, platinum boat, and platinum contacts are removed from the combustion tube, which is taken from the stand and placed in an upright position without removing it from the precipitation tube that covered it during the combustion. The prepared reagent of 10% sodium acetate solution and bromine in glacial acetic acid is poured into this precipitation tube (receiver *A*) and aspirated 1 to 2 cm. beyond the spiral of the combustion tube. With the mouth of the combustion tube closed with the index finger, the capillary end is placed in the Erlenmeyer flask (receiver *B*) containing the 20% aqueous sodium acetate solution; the combustion tube is clamped vertically to a stand, and the aspirated solution is allowed to drain into the Erlenmeyer flask. About 6 ml. of distilled water is placed in the precipitation tube (receiver *A*), aspirated into the combustion tube, and again transferred to the same Erlenmeyer flask. With the aid of a graduated wash cylinder the combustion tube is rinsed, while being rotated, with two more 6-ml. portions of distilled water, without removing the tube from the Erlenmeyer flask.

To destroy the excess of bromine 2 or 3 drops of formic acid is run down the wall of the Erlenmeyer flask and its contents are shaken. When the solution is decolorized, it is tested for free bromine by adding a trace of methyl red indicator solution. If the indicator is decolorized, free bromine is still present and another drop of formic acid is added. If the solution remains pink, 2 ml. of 10% potassium iodide solution and 5 ml. of 2 *N* sulfuric acid are added and the solution is left standing in the stoppered Erlenmeyer flask for five minutes. Then the iodine is quickly titrated with 0.01 *N* sodium thiosulfate solution to a faint yellow color; 4 to 6 drops of starch indicator solution is added, and the solution is finally titrated to a slight pink coloration.

| Time: | Minutes |
|--|---------|
| Weighing of the sample..... | 10 |
| Preparation and filling of the combustion tube..... | 25 |
| Combustion..... | 30 |
| Cooling of the combustion tube (during this time the reagents for the titration are prepared)..... | 20 |
| Transfer of the absorption liquid..... | 10 |
| Titration..... | 15 |
| Total..... | 110 |

Calculation:

Log of ml. 0.01 *N* sodium thiosulfate solution,
 Plus log of factor (32562),
 Plus negative log of weight of sample;
 Antilog of total = percentage iodine.

Remarks

Reviews and Reports. Existing methods for the determination of halogens in organic compounds have been extensively reviewed by F. Hernler and R. Pfenningberger (fluorine and chlorine, 399 papers);⁴⁸ T. Leipert (bromine, 122 papers;^{66a} iodine, 155 papers^{66b}); Th. v. Fellenberg (iodine, 42 papers);⁴³ and G. Lunde and co-workers (iodine, 46 papers).⁶⁷

Aside from these reviews numerous investigators have reported on the applications, modifications, difficulties, or deficiencies of existing micro methods for the determination of fluorine,^{51, 94} chlorine,^{6, 17, 26, 28, 30, 35, 60, 64, 78, 91, 105, 114} bromine,^{19, 26} and iodine,^{10, 21, 26, 29, 33, 37, 43, 45, 49, 52, 65-67, 69, 82, 84, 95} not only in pure organic compounds but also in biological material,^{6, 15, 29, 30, 43, 52, 64, 65, 69, 78, 94} food-stuffs,⁹¹ gasoline,¹⁰⁵ and perfumes.¹¹⁴

Wet Combustion Methods. For the quantitative determination of halogen in organic compounds the *Carius Method*^{24, 50, 71} possesses numerous advantages which have been successfully incorporated in the respective semi-micro²⁶ and micro methods.^{39, 80a, 87, 102, 104} The method offers a high degree of precision because its reagents are few and are easily purified and, therefore, no blanks have to be taken into consideration. Furthermore, the method involves extremely simple stoichiometric reactions. The objections to the micro-Carius method, such as the danger of explosions, the long heating period, and the possibility of contaminating the reaction product with glass splinters, previously somewhat justified, have been successfully overcome by J. B. Niederl and co-workers⁷⁴ through a combination of the early micro-Carius

method of F. Emich³⁹ with the subsequently devised method of F. Pregl^{80a, 87} and application of a method of differential weighing to the final reaction product. Through the reduction of the amount of nitric acid employed in the oxidation process the danger of explosions has been practically eliminated, while, by shortening the time of heating to one hour or less, the second objection has been overcome. The third difficulty, the possible contamination of the silver halide precipitate with glass splinters, has been remedied by first weighing the filter tube with the precipitate, then dissolving the precipitate with a saturated potassium iodide solution, followed by reweighing the filter tube, the difference in the weight of the filter tube then giving the weight of the pure silver halide.

The weighing and introduction of the sample contained in a silver foil cup,⁵⁶ replacement of the nitric acid by potassium hydroxide and potassium nitrate solutions,³⁴ volumetric determination of iodine by using mercuric nitrate instead of silver nitrate,³³ special methods of sealing and opening the pressure tubes,¹⁰⁴ and electrically heated furnaces⁶¹ have been described.

The *Dichromate Method* of M. K. Zacherl and H. G. Krainick¹¹⁵ is based upon the wet macro combustion method of H. Baubigny and G. Chavanne⁷ and its subsequent modifications by M. Berend,¹⁰ H. Dieterle,³² and others.^{76, 105} The method involves the use of concentrated sulfuric acid and a mixture of potassium and silver dichromate. It is one of the speediest of the halogen determination methods but has the disadvantage of limited application.^{98, 115} Utmost purity of the oxidizing and absorption reagents is essential.

Other wet combustion methods involve the use of *fuming sulfuric acid*,¹¹³ *potassium persulfate*,¹⁰¹ and *potassium permanganate*.^{11, 16, 90, 95} Suitable modifications allow the simultaneous determination of carbon,⁸⁵ of arsenic,²⁷ and of certain metals.¹¹³ The reaction product may be determined gravimetrically,^{85, 101, 113} volumetrically,¹¹⁵ or manometrically.¹⁰⁶

The macro *Alkaline Reduction Method* as devised by A. Stepanow⁹⁷ and others^{25, 63, 89, 107} has been adapted with appropriate modifications to the analysis of semi-micro and micro samples of reactive alkyl and aryl halides by W. H. Rauscher⁸³ and others.^{33, 42, 83, 103} Metallic sodium is used in most of these methods, although the use of calcium and lithium¹⁰³ also has been suggested. As solvent, low- and high-boiling alcohols,^{42, 97} ethanol amine,⁸³ dioxane,⁸³ as well as liquid ammonia^{25, 107} have been proposed. The halogen is usually determined gravimetrically, but alkalimetry³³ and also titration with the aid of suitable adsorption indicators^{41, 42} have been tried successfully.

Dry Combustion Methods. F. Pregl^{21, 44, 80a, 87} devised the *Catalytic Oxidation Method* for halogen which was modeled after the semi-micro method of M. Dennstedt.³¹ This method was modified by L. T. Hallett⁴⁷ for the continuous operation without interruption of the heating process. A quartz absorption tube is sealed vertically to the end of the combustion tube. The combustion gases are bubbled through the absorption liquid which, at the end of the combustion, is rinsed through a stopcock at the bottom of this absorption tube. A detachable spiral tube serving a similar purpose has been described by C. W. Beazley.⁹ By dry combustion in an atmosphere of oxygen *with*^{21, 31, 44, 47, 52, 70, 80a, 87} or *without*^{46, 58, 88, 93} the *platinum catalyzer*, potentiometric⁷⁰ and volumetric⁵² titration of the halogen, as well as titration involving the use of suitable adsorption indicators,^{17, 46, 58, 59, 88, 93} has proved to be applicable.

Hydrogenation Methods. The *Catalytic Hydrogenation Method* of M. Busch²⁰ and others^{14, 54, 86} was first converted to a semi-micro method by H. Ter Meulen and J. Heslinga,⁹⁹ and this in turn has been adapted to microchemical work by C. Weygand and A. Werner,¹¹² K. Bürger,¹⁸ and others.^{62, 96, 100} In all these methods the halogen present in the organic compound is converted to the respective hydrogen halide in the presence of hydrogen and a suitable catalyzer, which is then determined gravimetrically,^{18, 96} alkalimetrically,⁶² or by the Volhard method.^{18, 96, 110} Simultaneous determination of nitrogen as ammonia, and of halogen as silver halide, by catalytic hydrogenation has been shown to be feasible by D. Buttescu.²²

Fusion Method. A. Elek and co-workers^{37, 38} successfully transformed the bomb method of S. W. Parr⁷⁹ into an efficient micromethod. The reaction product is usually determined *gravimetrically*,³⁸ but may also be done volumetrically as with iodine,³⁷ or *colorimetrically*.⁷⁷ A semi-micro bomb method has been described by F. E. Beamish.⁸ In all these bomb methods purity of the reagents (sodium peroxide, etc.) is absolutely necessary, but difficult to attain.

The *Liebig Calcination Method*^{50, 71} has also been converted into a micro method by R. H. Kimball and co-workers.⁵⁶ The sample is weighed in a gelatin capsule and ignited in a Pyrex ignition tube containing lime. After the ignition the contents of the tube are dissolved in nitric acid and the halogen determined by the Volhard titration method.¹¹⁰ Wm. M. MacNevin and Wm. H. Baxley⁶⁸ use a steel bomb instead of the Pyrex glass ignition tube. Application of the alkali fusion method to the determination of iodine, particularly in biological material, is favored by Th. v. Fellenberg,⁴³ E. C. Kendall,⁵⁵ and numerous others.

Ionizable halogen in organic compounds (quaternary ammonium halides, etc.) may be determined by the method of A. Schlömer,⁹² or S. Kamio and H. Sakamoto.⁵³ The sample is dissolved in water or aqueous alcohol and is then titrated with 0.01 *N* silver nitrate solution for chlorine, 0.02 *N* silver nitrate solution for bromine and iodine, 0.1% bromophenol blue, 0.1% dichlorofluorescein, or 0.2% fluorescein solution respectively, being used as indicators.

Determination of bromine alone in the presence of chlorine¹² and iodine,¹¹¹ as well as simultaneous determination of both these elements⁷² is possible. A method for the *simultaneous determination of chlorine and bromine* has been devised by L. Moser and R. Miksch.⁷² It utilizes the thermal dissociation of ammonium chloride and bromide, and is carried out as follows:

The silver halide precipitate, as obtained by any of the previously described methods, is collected in a Neubauer microcrucible, which is described in the determination of sulfur on p. 194. The crucible is dried in the aluminum block at 150° C., is left to cool on the metal block of the microdesiccator, and weighed. Dry ammonium iodide, free from non-volatile residues, is added to the crucible, in an amount about six times the weight of the precipitate; the crucible is heated at 250 to 300° C., first covered and then open, in a muffle or in the aluminum block, until the ammonium halides have completely volatilized. The crucible is allowed to cool in the microdesiccator and then is weighed. To check the constancy of weight, the heating with ammonium iodide is repeated.

From the weight of the silver chloride and bromide precipitate (first weighing) and the silver iodide formed by the heating with ammonium iodide (second weighing), the chlorine and bromine content of the substance is calculated. The indirect determination of chlorine and bromine when both are present can be carried out with an accuracy of about $\pm 0.5\%$. Ammonium bromide may be substituted for ammonium iodide.

Modifications in the conventional *iodine* methods involve photometric⁴⁰ and also nephelometric² determinations. As standards in iodometric titrations, aside from potassium biiodate,^{4, 10, 37} ceric sulfate⁴⁹ and the sodium salt of acetomercury thymol¹³ have been suggested.

The conventional Pregl *filter tube*^{23, 80a, 87} has been improved by the introduction of a sintered-glass filter plate which, however, has to be tested for proper retentivity.⁷⁴ Substitution of the filter tube by a Gooch crucible of proper dimensions,³⁶ or by the Schwarz-Bergkampff type of filter beaker,¹ has also been attempted.

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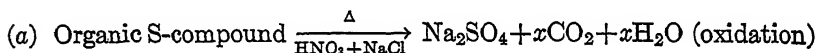
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VII. DETERMINATION OF SULFUR

GRAVIMETRIC WET COMBUSTION (CARIUS) METHOD

Principle

The organic sulfur compound is oxidized by *wet combustion* in the presence of concentrated nitric acid and sodium chloride at a temperature between 280 to 300° C.^{10, 15, 40, 44, 46, 59} The sulfur present is thus oxidized to sulfuric acid, which in turn reacts with the sodium chloride to yield sodium sulfate. After dilution and filtration the sodium sulfate is converted to barium sulfate, which is filtered by inverted filtration. After ignition the barium sulfate is weighed with both crucible and immersion filter.



Apparatus

Furnace (Fig. 56),^{35, 40, 44, 46} *Pressure Tubes*. These are the same as used in the corresponding *wet combustion method* for the determination of halogen.

Filter Funnel. An ordinary funnel of Pyrex glass having a diameter of 5 cm. at the top and a stem 4 cm. long and 7 to 8 mm. in diameter will serve the purpose.

Evaporation Apparatus (Fig. 44).⁴⁰ This apparatus consists of a precipitation or evaporation tube (a) of 15-cm. length and 3-cm. outside diameter, having a No. 7 interchangeable ground-glass joint. This joint carries the ground-glass head (b), which has a horizontal inlet tube 5 cm. long and 6 mm. in outside diameter; this inlet tube is bent at a right angle where it is sealed to the head and continues vertically for a length of 19 cm., ending in a capillary of 0.5-mm. inner diameter; the outlet tube of this head is 4 cm. long, 6 mm. in outside diameter, and is connected by means of the T-tube (c) and a suitably bent glass tubing to the side-arm suction tube (d), which serves as a suction flask as well as a trap. Attached to the inlet tube is a capillary tubing in

which is placed a tightly compressed plug of glass wool to prevent particles of dust from entering the evaporation tube during the process of evaporation; a wad of glass wool is also inserted into the orifice of the outlet tube. The heating bath (e), which is a 1-liter beaker of Pyrex glass containing a saturated salt solution to raise the boiling

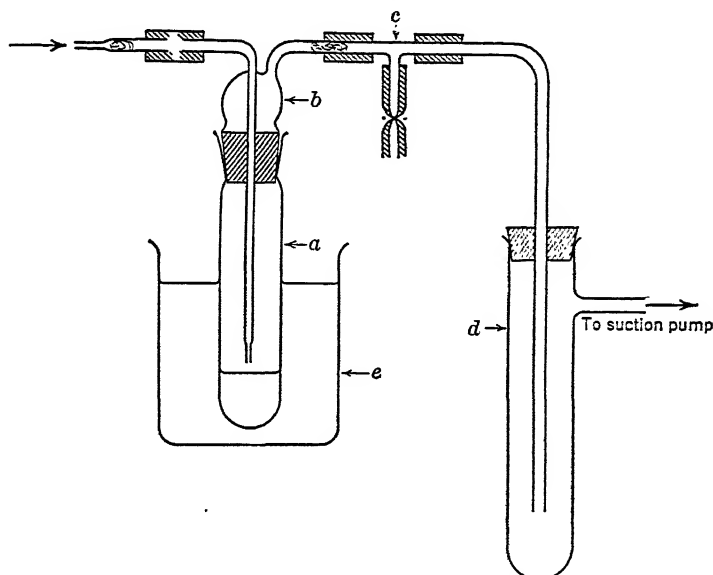


Fig. 44. Evaporation Apparatus. Explanation in Text.

point of water to 105–110° C. in order to speed up the evaporation, completes the apparatus.

Porcelain Crucible and Immersion Filter (Fig. 45).^{15,16, 50} The crucible has a capacity of about 15 mL., is 3.5 cm. high, and has a diameter of 2.8 cm. at the top and 2.2 cm. at the bottom; the inside is glazed black. The immersion filter is also made of porcelain, is 5 cm. long, and has a porous filter plate of 1-cm. diameter; its stem has an outside diameter of 3 mm., and a bore of 1 mm.

*Preparation of the Porcelain Crucible and Immersion Filter.*⁵⁰ To bring the crucible and immersion filter to constant weight, they have to be properly treated. A new crucible is rinsed repeatedly with alcohol and distilled water and then it is wiped inside as well as outside with a clean lint-free cloth; the immersion filter is cleaned by siphoning through 50 mL. of 10% hydrochloric acid solution, which is followed by an equal volume of distilled water which, however, is siphoned through in both directions. A used crucible is cleaned of precipitate from

previous analyses by wiping its inside with a cotton wad wound around a toothpick—the knurled iron wire cannot be used because of the possibility of scratching the glazed surface—and then is rinsed repeatedly with distilled water; the outside of the crucible is wiped with a clean lint-free cloth. The immersion filter is freed of precipitate by gently brushing the porous plate with a small brush and then siphoning through distilled water in both directions. Washing with hot concentrated sulfuric acid should be resorted to only in extreme cases. The immersion filter, after being disconnected from the suction pump and its stem wiped with a clean cloth, is placed in the crucible where it remains during the entire procedure of drying, igniting, cooling, and weighing, which is



FIG. 45. Crucible and Immersion Filter.

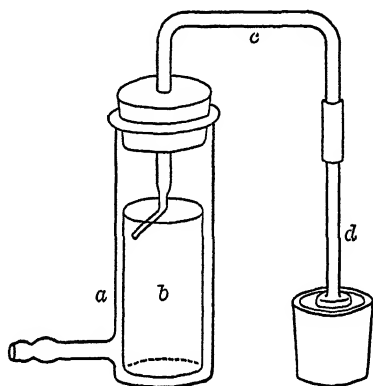


FIG. 46. Apparatus for the Inverted Filtration. Explanation in Text.

precisely the same before as after an analysis, and is described in detail in the paragraph on drying and igniting. The procedure of washing, drying, igniting, and weighing the crucible and immersion filter is repeated, and the result should agree within ± 10 micrograms with the first weighing. They are counterpoised with a ground-glass-stoppered tare bottle containing lead shot.

Suction Flask (Fig. 46). The suction bottle (a) is a flat-bottomed glass tube 11 cm. long and 4 cm. in diameter with a tubulature at the bottom, by which it is connected with a rubber tubing to the suction pump. This rubber tubing is intersected by a glass T-tube, the vertical arm of which is provided with a short rubber tubing carrying a pinch clamp for the regulation of the speed of filtration. A flat-bottomed test tube (b), 7 cm. long and 2.5 cm. in diameter, is placed inside the suction bottle to collect the filtrate, so that the filtration may be repeated if necessary. The siphon (c) is a capillary glass tubing of 5-mm. outside

diameter and 1-mm. bore. The arm which extends through a rubber stopper into the suction bottle is 9 cm. long and ends in an oblique capillary tip; above the rubber stopper it is bent at a right angle to continue horizontally for 7 cm. and then it is bent again to form a vertical arm 5 cm. long, which is also drawn out to a capillary tip having the same outside diameter as the stem of the immersion filter. The immersion filter (*d*) is connected to this tip with a short piece of flexible rubber tubing, while the porous filter plate extends into the crucible.

Reagents

All reagents must be free of sulfur, sulfide, sulfite, and sulfate ions.

Concentrated Nitric Acid (sp. gr.: 1.42).

Concentrated Hydrochloric Acid (sp. gr.: 1.19).

Dilute Hydrochloric Acid (1 : 300).

Sodium Chloride. Reagent quality.

Barium Chloride. C.P. crystals.

Barium Chloride Solution (10%). Prepared by dissolving 10 grams of barium chloride in 100 ml. of distilled water.

Ethyl Alcohol (95%).

Distilled Water.

Procedure

Preparation and Weighing of the Sample. Solids are weighed in the weighing tube; semi-solids such as waxes, fats, and syrups in open capillaries; and liquids in weighing pipets (pp. 44-46). Again, the amount of sample to be taken depends upon the precision of the available balance.

Filling the Pressure Tube. Dry solids are transferred directly into a clean and dry pressure tube. Semi-solids or liquids are introduced in capillaries or capillary pipets; depending upon the reactivity or volatility of the compound it is introduced either before or after the nitric acid. A spatula point of sodium chloride, that is, between 10 and 15 mg., is added to the reaction material.

The *sealing of the pressure tube*, the *digestion process*, and the *opening of the pressure tube* are carried out as described in the corresponding halogen determination method (p. 155), except that the digestion period is extended to two hours.

Transfer of the Reaction Product. The oxidation mixture is diluted with 3 ml. of distilled water, and the resulting solution is filtered through a small funnel, having a small moistened cotton wad as a filter mat, into the precipitation tube of the evaporation apparatus (Fig. 44).

The same part of the pressure tube is again filled with distilled water, which is also filtered through the same funnel and collected in the precipitation tube. Then the upper part of the pressure tube, with the open tip facing downward into the funnel, is filled with distilled water, and this washing is also filtered into the precipitation tube. Finally, the lower part of the pressure tube is filled once more with distilled water, which is filtered and collected as before.

Evaporation of the Sulfate Solution. The filtered sulfate solution collected in the precipitation tube, which, with the washings, will have a volume of 10 to 12 ml., has to be evaporated to dryness. This is conveniently accomplished with the aid of the evaporation apparatus shown in Fig. 44. The precipitation tube containing the sulfate solution is attached to the distillation head of the apparatus and then is immersed in a concentrated salt solution contained in a suitable beaker. After the rest of the apparatus has been assembled, as shown in the illustration, suction is applied; the solution in the beaker is brought to boiling, and after ten to fifteen minutes the contents of the precipitation tube will have been evaporated to dryness.

Transfer of the Sulfate. To the dry residue in the precipitation tube is added 3 ml. of distilled water, and the resulting solution is poured without loss, which is accomplished by slightly greasing the outer rim of the precipitation tube, into the previously weighed porcelain crucible. The precipitation tube is rinsed with three successive portions of 2 ml. of distilled water, and these washings are added to the liquid in the crucible. During this operation the immersion filter remains in the crucible.

Precipitation. The porcelain crucible is placed on a steam bath, the opening of which has been covered with a cloth to protect the crucible from coming in contact with the metal ring of the bath. The crucible is heated on the steam bath for five minutes; then 0.5 ml. of 10% barium chloride solution is added drop by drop; after the crucible has stood on the steam bath for another five minutes it is placed on a clean glass surface, covered with a beaker, and allowed to cool for five minutes.

Filtration. The previously cleaned flat-bottomed test tube * is placed in the suction bottle and the rubber stopper carrying the siphon is inserted. After the stem of the immersion filter is attached to the capillary tip of the siphon sufficient suction is applied so that the solution filters at a rate of 1 or 2 drops per second. After the aqueous solution

* It is important that a clean test tube be used, because it is advisable to observe whether particles of the filtrate are passing through the immersion filter; if this is the case, the filtrate collected in the test tube is transferred to the crucible and the filtration is repeated.

has been filtered off, the barium sulfate precipitate in the crucible is washed three times with 3 ml. of dilute hydrochloric acid solution (1 : 300) by spraying the wash liquid on the immersion filter and the wall of the crucible, from the rim on downward, while rotating it, so that no part of it is neglected. These washings are also filtered off through the immersion filter as before. Then, without being removed from the crucible, the immersion filter is detached from the capillary end of the siphon and is placed in the crucible, where it remains during the entire process of heating, igniting, and weighing.

Drying and Ignition. After the completion of the filtration the upper part of the stem of the immersion filter and the outside of the crucible are wiped with a clean lint-free cloth, after which it is handled only with the crucible tongs. With the immersion filter remaining in the crucible, it is transferred to a drying oven and heated for five minutes at a temperature of about 120° C. Then it is placed in a larger porcelain crucible provided with a cover, set on a clay triangle, and heated with a gas burner to a dull red.* The heating is continued for five minutes, after which the porcelain crucible is removed from the large crucible, placed on a metal block (the metal block of a micro-desiccator will serve this purpose), covered with a beaker, and after five minutes the crucible is transferred to the conical cavity of a micro-desiccator. After another five minutes the crucible is placed into a second microdesiccator, left standing near the balance for ten minutes, and then crucible and immersion filter are weighed together to within ± 10 micrograms.

| Time: | Minutes |
|--|---------|
| Weighing of the sample | 10 |
| Preparation, filling, and sealing of the pressure tube. . | 15 |
| Digestion | 120 |
| (During this time the crucible is dried, ignited, and weighed) | |
| Transfer and evaporation of the oxidation mixture.... | 20 |
| Precipitation..... | 15 |
| Filtration | 10 |
| Drying and igniting..... | 15 |
| Cooling and weighing of the crucible and immersion filter | 30 |
| Total..... | 235 |
| Waiting time during digestion..... | 120 |
| Net..... | 115 |

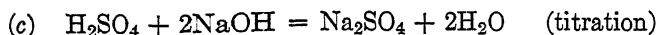
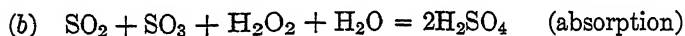
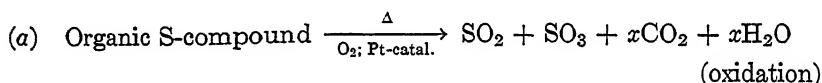
* Instead of a gas burner an electric furnace may be employed, but the temperature of the furnace must be high enough to heat the large crucible, which contains the crucible with the barium sulfate precipitate, to a dull red.

Calculation:

Log of weight of barium sulfate,
 Plus log of factor (13782),
 Plus negative log of weight of sample;
 Antilog of total = percentage of sulfur.

TITRIMETRIC DRY COMBUSTION METHOD**Principle**

The organic substance containing sulfur, but not containing halogen or nitrogen, is oxidized in an atmosphere of oxygen in the presence of a platinum catalyst.^{12, 17, 44, 46} The sulfur present in the compound is thereby converted into the gaseous oxides of sulfur, which are then absorbed in aqueous hydrogen peroxide solution distributed over a spiral condenser. Thus the final sulfur oxidation product is sulfuric acid, which is titrated with 0.01 *N* sodium hydroxide solution.

**Apparatus**

Oxygen Tank, Gas Wash Bottle, Combustion Spiral Tube, Combustion Stand, Platinum Contacts. These are the same as in the *dry combustion method* for the determination of halogen (p. 160).

Titration Equipment. This is the same as described under "Standard Solutions" (p. 51).

Reagents

Perhydrol (30%).

Hydrogen Peroxide Solution. Twenty milliliters of 30% perhydrol is diluted with distilled water to 100 ml. total volume.

Distilled Water.

0.01 N Sodium Hydroxide Solution (p. 56).

Methyl Red Indicator Solution (p. 54).

Procedure

Combustion. The combustion tube is cleaned and dried as described on p. 162. Ten milliliters of hydrogen peroxide solution, previously neutralized with 0.01 *N* sodium hydroxide solution to a canary yellow,

is poured into a clean test tube and siphoned about 1 cm. beyond the spiral of the combustion tube. After the spiral has been completely moistened with the absorption liquid by rotating the combustion tube, the excess is permitted to drain off into the test tube and is discarded. Then the combustion tube is placed on the stand, the pre-ignited platinum contacts and the rubber stopper are inserted, and the pieces of wire gauze are slipped over the combustion tube. The part of the tube containing the spiral is protected by placing a precipitation tube over it which is held in position by clamping it to a small stand. Next, the combustion tube is connected to the gas wash bottle and the oxygen tank, and the flow of oxygen is regulated to a delivery of 3 ml. per minute, as described in the corresponding halogen determination on p. 163. Then the long burner is lighted and the platinum contacts are heated to a dull red.

The amount of substance to be taken depends upon the precision of the balance and also upon the percentage of sulfur present in the compound, but enough should be taken to obtain a precipitate weighing 4 to 5 mg. if it is weighed on a microanalytical balance and about twice as much if an ordinary analytical balance is employed. The sample, if a solid, is weighed in the platinum boat; if a liquid, in a capillary pipet which is placed in a platinum foil; it is placed in the combustion tube 6 to 7 cm. from the nearest platinum contact. The combustion is started about 5 cm. from the substance with a slightly hissing flame of a gas burner which is slowly moved towards the sample until the first sign of decomposition of the substance is noticed. The burner is left in this position for ten minutes and then is gradually moved nearer to the sample. The gradual advance of the burner is important, because, if the combustion is carried out too rapidly, uncombusted material may be deposited before the indentation in front of the spiral of the combustion tube. The heating is continued for ten minutes directly under the substance and then the burner is gradually moved forward until it reaches the long burner. The time required for the entire combustion is approximately forty minutes for an average sample and up to one hour for a larger one. After completion of the combustion both burners are extinguished and the combustion tube is allowed to cool in a stream of oxygen. Then the oxygen is turned off, the combustion tube is detached from the gas wash bottle, and the wire gauzes as well as the platinum boat, or foil, and the platinum contacts are removed.

Titration. Eight milliliters of distilled water is placed in the precipitation tube which covered the spiral of the combustion tube, the mouth of which has been provided with a dust filter. This wash liquid is siphoned into the combustion tube to 2 cm. beyond the end of the

spiral. The dust filter being closed with a finger, the outlet of the combustion tube is placed in a 125-ml. steamed-out Pyrex glass Erlenmeyer flask, and the wash liquid is allowed to drain off. This procedure of rinsing the combustion tube is repeated twice with the same amount of wash liquid, which is also collected in the Erlenmeyer flask. Then the combustion tube is rinsed once more with about 5 ml. of distilled water, which is sprayed into the orifice of the combustion tube, but this solution is permitted to drain into the precipitation tube, where it is tested for its acidity by adding a trace of methyl red. If, after 1 drop of 0.01 *N* sodium hydroxide solution has been added, the solution turns yellow, indicating that the previous three washings were adequate, as they usually are, then it may be discarded; otherwise it is added to the washings in the Erlenmeyer flask. The solution in the Erlenmeyer flask is boiled for about twenty seconds, another trace of methyl red is added, and then it is titrated with 0.01 *N* sodium hydroxide solution to the end point, which is reached when the solution retains the canary-yellow color for two minutes.

| Time: | Minutes |
|--|---------|
| Weighing of the sample..... | 10 |
| Preparation and filling of the combustion tube..... | 20 |
| Combustion..... | 40 |
| Cooling of the combustion tube *..... | 15 |
| Transfer and titration of the absorption solution..... | 20 |
| Total..... | 105 |

Calculation:

Log of ml. 0.01 *N* sodium hydroxide solution,
 Plus log of factor (20493),
 Plus negative log of weight of sample;
 Antilog of total = percentage of sulfur.

* During this time the next sample can be weighed.

Remarks

Wet Combustion Methods. The time-honored wet combustion method for the determination of sulfur in organic compounds as originally devised by L. Carius^{10, 26, 38} and as first applied to quantitative micro work by F. Emich and J. Donau¹⁵ has been given preference^{1, 36, 40, 56, 57} over both the dry combustion^{12, 17, 24, 44, 46} and the fusion methods.^{6, 14, 41} The wet combustion method, which may also be used in semi-micro work,¹¹ is applicable to any and all types of organic sulfur compounds, regardless whether they are very volatile or not volatile

at all, and regardless whether in addition to sulfur the substance also contains other elements, such as halogen or nitrogen, or both. The reagents used are easy to purify, and no blank is necessary. The previously often-voiced objection to the Carius method, namely the danger of explosion and the possibility of contaminating the barium sulfate precipitate with glass splinters, have been remedied,⁴⁰ the first by reducing the amount of nitric acid used to only a few drops, and the second by filtering the sulfate solution before precipitation. Usually the sulfate is precipitated as *barium sulfate*, but precipitation with benzidine hydrochloride has also proved to be feasible. In the latter case a regular halogen filter tube (p. 152) is used for the filtration, drying and weighing of the *benzidine sulfate* precipitate.^{40, 59} The evaporation of the sulfate solution to dryness is best accomplished under reduced pressure and in a closed system;⁴⁰ evaporation over free gas flames, or on open steam baths heated by gas, must definitely be avoided.³⁶ Digestion of non-volatile sulfur compounds in Kjeldahl flasks^{4, 29, 32, 48, 49} has been tried, and either potassium hydroxide in combination with hydrogen peroxide^{32, 49} or potassium permanganate⁴ as well as chlorates and iodates^{28, 29} may be used as oxidizing agents.

A. Friedrich¹⁷ has described a gravimetric method for the simultaneous determination of *sulfur* and *halogen*, utilizing the wet combustion method. The organic substance is oxidized in the pressure tube with nitric acid to which a crystal of silver nitrate has been added. The filtrate obtained after filtration of the silver halide precipitate and the washings are collected in a short test tube, rinsed quantitatively into a Pyrex glass dish, and the sulfuric acid is precipitated on a steam bath with 2 to 3 ml. of a 1% solution of barium nitrate. This solution must be tested for halogen with silver nitrate. If it should not be free from halogen, it must be precipitated from the warm solution with silver nitrate and the filtrate added to the solution in the dish. The transfer and filtration of the barium sulfate precipitate are carried out by any of the standard methods. Distilled water is used in the washing procedure instead of the dilute acid solutions.

Dry Combustion Methods. The catalytic dry combustion method for the determination of halogen and sulfur as devised by F. Pregl^{44, 46} has been modeled after the semi-micro method of M. Dennstedt.¹² In this method the final oxidation product may be determined *gravimetrically* in all cases, and *titrimetrically* if no interfering elements such as halogens, or nitrogen, or both, are present. The *gravimetric* determination is carried out as follows:

After the combustion, which is carried out as described on p. 188, the combustion spiral tube is removed from the stand, and its upper

part is wiped with a towel. Then it is held in a vertical position, and with the aid of the graduate wash cylinder 3 ml. of dilute hydrochloric acid solution (1 : 300) is sprayed into the orifice of the tube while it is rotated to ensure effective rinsing of its inner surface. To avoid possible loss of absorption liquid during the rinsing, the capillary end of the combustion tube is held over the porcelain crucible. The mouth of the combustion tube is closed with a dust filter, and the tube is held in an inclined position while the absorption liquid is blown into the porcelain crucible; the capillary tip is also rinsed with a few drops of dilute hydrochloric acid solution. The washing of the combustion tube is repeated three times, but with 2 ml. of dilute hydrochloric acid solution, which is also collected in the porcelain crucible. Then it is washed once more with 3 ml. of wash liquid, and this solution is drained into the test tube which served as a cover for the combustion tube during the combustion. A drop of barium chloride solution is added to this wash liquid, and it is observed whether turbidity occurs or not. If an opalescence or precipitate is noted, the liquid is transferred to the porcelain crucible after the original solution therein has been evaporated. The precipitation, filtration, and ignition of the barium sulfate precipitate are carried out as described on p. 186. With proper modifications, such as extraction of the residue left in the boat after combustion, organic metal salts containing sulfur may be analyzed satisfactorily.²

A combustion spiral tube in which the *spiral tube* is *detachable* has been described by C. W. Beazley.⁷ An arrangement for *continuous operation* without interruption of the heating process has been devised by L. T. Hallett and J. W. Kuipers.²⁴ The combustion gases are bubbled through the usual hydrogen peroxide solution contained in a suitably constructed absorption tower. At the termination of the combustion process the sulfate solution is rinsed through a stopcock at the bottom of the vertical absorption tower into the appropriate titration or precipitation vessel. The combustion may be carried out with^{12, 17, 44, 46} or without the platinum contacts.^{23, 33, 47, 51}

According to E. W. D. Huffman²⁷ the organic substance containing sulfur may also be combusted in an atmosphere of oxygen in a combustion tube containing *metallic silver*. After combustion, the silver sulfate is extracted and the resulting extract is subjected to electrolysis. From the weight of the silver deposited the amount of sulfur originally present in the organic compound may be calculated. Carbon and hydrogen may be determined simultaneously. An *electrolytic oxidation* method for the determination of sulfur in organic compounds has been described by P. Piutti and D. Dinelli.⁴³

As with halogens, it is also possible to determine sulfur in organic compounds by destructive *catalytic hydrogenation*, according to H. Ter Muelen and J. Heslinga.⁵⁵ The sulfur present is thus converted into hydrogen sulfide, which then may be determined gravimetrically or iodometrically.²⁰

Fusion Methods. In the *microbomb method* of A. Elek and D. W. Hill,¹⁴ which is particularly useful for the determination of sulfur in proteins, and which is modeled after the method of S. W. Parr,⁴¹ the organic sulfur compound is fused with a mixture of potassium nitrate, or chlorate, and sodium peroxide, and sugar in a suitably constructed metal bomb (Fig. 42).^{2, 6, 14, 41} These oxidizing agents ensure quantitative oxidation of the sulfur to sulfuric acid or alkali sulfates, respectively. The sulfate thus formed is precipitated with barium chloride and the resulting barium sulfate precipitate is determined gravimetrically.

The reagents must be free from sulfur, sulfides, sulfites, or sulfates. The fusion and extraction is carried out as in the corresponding halogen determination described on p. 166. The resulting extract is cooled in an ice bath, and then 5 ml. of concentrated hydrochloric acid is slowly added. The acid solution is filtered, and both test tube and filter are rinsed with distilled water. The filtrate is transferred in 10- to 15-ml. portions to a well-steamed 50-ml. round-bottomed Pyrex glass dish or platinum evaporating dish with a spout; 0.5 ml. of barium chloride solution is added to the liquid in the dish, and the whole is evaporated to dryness. The solid residue is moistened with 10% hydrochloric acid solution, and the evaporation is repeated. The final solid residue is taken up in 30 ml. of distilled water and allowed to stand over night. The procedure of transferring the barium sulfate depends upon whether inverted filtration or filtration by gravity is employed.

Fusion of the organic sulfur compound with sodium peroxide in a *nickel* crucible covered with a weighted lid gives satisfactory results with non-volatile sulfur compounds, but may lead to serious explosions.^{34, 45} Also fusion in an *open boat* in presence of a sodium carbonate-cobalt oxide oxidation mixture and in an atmosphere of oxygen has been found to be feasible.^{8, 62}

Filtration. For the filtration of the barium sulfate precipitate several methods have been devised.^{5, 13, 15, 16, 25, 31, 39, 44, 46, 50, 61} At present the method of *inverted filtration* as originally devised by F. Emich,^{15, 16} which subsequently was applied to the filtration of barium sulfate precipitates originating in organic sulfur determinations by W. Saschek,⁵⁰ and others,^{25, 39} is the simplest and has now become a standard procedure. The barium sulfate precipitate may, however, also

be filtered using a regular suction arrangement and a Neubauer crucible.^{44, 46} In this case the apparatus (Fig. 47) consists of a 250-ml. suction flask (a) fitted with a rubber stopper through which a glass tube (b) of 8-cm. length and 1-cm. outside diameter is inserted. The glass tube should have the same outside diameter as the bottom of the Neubauer crucible.

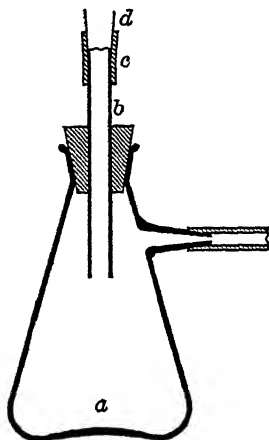


FIG. 47. Filtration Apparatus for Filtration with the Neubauer Crucible.
Explanation in Text.

A rubber tubing 2 cm. long is placed over the top of the glass tube to form a sleeve (c) which holds the crucible (d) in place. A rubber tubing approximately 50 cm. long is attached to the side arm of the suction flask; the free end of the rubber tubing is provided with a glass mouthpiece, because the filtration is carried out with suction by mouth.

*Neubauer Platinum Crucible.*³ The crucible is provided with a lid and a capsule which fits tightly over the bottom. It has a capacity of approximately 3 ml., is 1.4 cm. high, and has a diameter of 1.2 cm. at the rim and 1 cm. at the bottom. The filter mat consists of compressed platinum sponge which, even at a high rate of filtration, completely retains the barium sulfate precipitate. A satisfactory working crucible should permit the passage of an average of 4 ml. of filtrate per minute if suction by mouth is applied.* The inside of the crucible is wiped

before every determination with a moist cotton tuft wound around a toothpick (not steel wire) and is repeatedly rinsed with distilled water; it is then placed in the rubber sleeve of the filtration device and washed well with dilute hydrochloric acid. After being removed from the filtration device it is closed with the lid and lower cap, placed on a platinum foil about 3 cm. square, and both are set in a silica triangle. The crucible is first dried on a hot plate or in a drying oven. When dry, the crucible is heated to redness for three minutes with a non-luminous gas flame. The lid is also held in the flame with the platinum-tipped forceps just long enough to heat it to redness. Then the crucible is allowed to stand on a clean metal block for five minutes, after which

* When the filtration becomes too slow, owing to the accumulation of barium sulfate in the pores of the filter mat, the crucible is washed with a small amount of concentrated sulfuric acid. After the crucible has been cleaned in this manner, freshly precipitated barium sulfate is again filtered onto the filter mat which, by means of suction, is rinsed repeatedly with distilled water to ensure that the pores of the filter mat have the proper density.

it is placed on the metal block of the microdesiccator and is weighed fifteen minutes later to ± 10 micrograms.

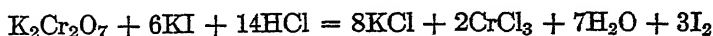
The time of cooling may be shortened by transferring the crucible to a second metal block several minutes later; the crucible can then be weighed ten minutes after the ignition.

The barium sulfate precipitate may be transferred from the precipitation tube to the Neubauer crucible by means of a dropping pipet provided with a rubber cap⁴⁶ or by a medicine dropper.⁵⁰ The dropping pipet is about 8 cm. long over all, 1 cm. in diameter, and narrows abruptly to a capillary of 3-cm. length and 1-mm. bore. After the transfer of the precipitate and the wash liquid, the rubber cap is removed and the pipet is alternately rinsed with alcohol and distilled water.

The barium sulfate precipitate may also be transferred to the crucible by means of a snipe feather cemented with Krönig's glass cement into a glass capillary 2.5 mm. in external diameter and approximately 15 cm. long.^{44, 46} Particles of the cement which adhere to the outside of the capillary are removed with benzene, and then the feather is washed consecutively with benzene, alcohol, and ammoniacal soap solution. The feather is kept in a stoppered test tube.

A new filtration method has been devised by P. L. Kirk and R. Craig³¹ for the filtration of very small amounts of precipitate. O. Wintersteiner⁶¹ has described an automatic filtration apparatus. A new filter crucible and⁵ a micro Gooch crucible¹³ have also been devised.

Titration. Titration methods may be employed for both the combustion and the fusion methods. Such titration methods²² may involve benzidine,¹⁷ barium chloride,^{32, 49} barium chromate,⁴ barium carbonate, barium oxalate, or lead nitrate. Straight *alkalimetric* determinations^{18, 21, 32, 44, 46, 49} as well as *iodometric* titrations^{4, 20, 21, 28, 37, 58} are in vogue, for the wet,^{4, 32, 49, 58} the dry,^{18, 21, 44, 46} and also the catalytic hydrogenation methods.⁵⁵ *Iodometric* titrations usually involve precipitation of the sulfate with an excess of standard barium chloride solution, followed by precipitation of the excess barium chloride with a standard bichromate solution and final *iodometric* determination of the excess bichromate as follows:



The use of suitable *absorption indicators*^{23, 24, 30, 33, 42, 47, 51-53, 60} such as tetrahydroxyquinone²⁴ or erythrosine⁹ is advocated more and more and has been found particularly useful in industrial work where large numbers of sulfur analyses have to be performed.^{24, 33, 47}

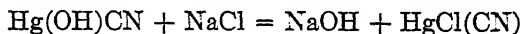
Since the *alkalimetric* sulfur determination method as devised by F. Pregl ^{44, 46} is applicable only to substances free of nitrogen or halogen, attempts have been made to devise titrimetric methods which eliminate this disadvantage. In the method of A. Friedrich and O. Watzlaweck ¹⁸ the initial combustion is carried out catalytically; the absorption solution and the washings are collected in a platinum or quartz dish. After the addition of 1 drop of phenolphthalein to the solution 0.02 *N* sodium hydroxide solution is run in from a buret with constant stirring until a permanent red color is obtained, whereupon the solution is concentrated on the steam bath. After twenty to thirty minutes the concentrated sodium sulfate solution is removed from the steam bath and 0.02 *N* sulfuric acid solution is run in from a buret, an amount equivalent to the 0.02 *N* alkali previously taken being used. The solution is stirred well with a glass rod after the addition of the sulfuric acid and again evaporated to dryness on the steam bath. The residue is dissolved in a little water, sprayed in a thin stream from a wash bottle along the edge of the dish, and again evaporated completely to dryness. The crust of salt is dissolved once more in water and the residue is allowed to stand for forty-five minutes on the steam bath. Repeated evaporation (three times) is essential to drive off the volatile acids and to convert the sulfuric acid originally present to sodium bisulfate. The residue is then dissolved in 5 to 8 ml. of hot water, a trace of methyl red indicator solution is added, and the solution is titrated with 0.02 *N* sodium hydroxide to the first appearance of the yellow color; the dish is then placed on the steam bath for a few minutes and the solution is titrated while still hot to the canary-yellow color.

Owing to the uncertainty whether or not all volatile acids have been completely removed from the bisulfate solution, a blank titration must be made, which, if negative, may be omitted in further analyses of the same or similar substances.

For the blank test, an amount of 0.02 *N* sulfuric acid equivalent to the total alkali used for the neutralization and for the bisulfate titration is run into the dish containing the sodium sulfate. The contents of the dish are evaporated to dryness on the steam bath; the residue is dissolved in water, allowed to remain on the steam bath for forty-five minutes, and titrated as above with 0.02 *N* alkali. If all the volatile acids have been removed in the first determination, the sulfuric acid used in the blank test will be titrated back fully; otherwise, a proportionately smaller amount of acid will be found.

Substances containing iodine cannot be determined by this method. An analysis requires three to four hours and is claimed to be accurate to $\pm 0.2\%$.

D. J. Gibson and T. H. Caulfield²¹ also reported a method by which sulfur and halogen may be determined simultaneously. The combustion products are absorbed in excess standard alkali, and the unused standard solution is titrated back. Mercuric oxycyanide is then added, and the halogen is determined by titration with 0.01 *N* sulfuric acid solution, methylene blue-methyl orange indicator solution, which permits the observation of the end point more easily than the ferric thiocyanate ordinarily employed, being used. The reaction involved proceeds as follows:



LITERATURE

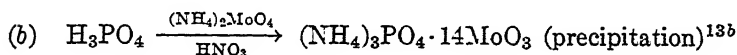
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VIII. DETERMINATION OF PHOSPHORUS

Principle

The organic substance is decomposed either by fusion with suitable solid oxidation mixtures or by digestion with a mixture of perhydrol and concentrated sulfuric acid. The phosphorus present in the organic substance is converted to phosphoric acid, which is determined gravimetrically as *ether-dried* ammonium phosphomolybdate.¹²



Apparatus

Precipitation Tubes. Pyrex glass test tubes approximately 100 ml. in total capacity, about 4.5 cm. in diameter, and 20 cm. high, and with markings at 15-ml. and at 30-ml. levels, are used.

Filter tubes. These are the same as described in the Carius method for the determination of halogen (p. 152). If a sintered-glass filter tube is used, it should be tested for its retentivity of the ammonium phosphomolybdate precipitate.

Filtration Apparatus. This is the same as described in the Carius method for the determination of halogen (p. 153).

Wash Bottles. One wash bottle each for alcohol, ether, acetone, ammonium nitrate solution, and distilled water is required.

Vacuum Desiccator.

Kjeldahl Digestion Flasks. These are the same as described under "Volumetric Determination of Aminoid Nitrogen" (p. 71).

Digestion Oven. This is the same as described under "Volumetric Determination of Aminoid Nitrogen" (p. 70).

Silver Crucible. This crucible is 1.8 cm. in lower and 3.3 cm. in upper diameter and is 4 cm. high.

Bomb. This is the same as is used for the corresponding halogen determination (p. 165).

Reagents

Ammonium Nitrate. C.P.

Ammonium Sulfate. C.P.

Ammonium Molybdate. C.P.

Sodium Peroxide. C.P.

Potassium Hydroxide. C.P.

Potassium Nitrate. C.P.

Sucrose, C.P., or d-Glucose, C.P.

Concentrated Nitric Acid (sp. gr.: 1.36).

Dilute Nitric Acid (1 : 1).

Concentrated Sulfuric Acid (sp. gr.: 1.84).

Perhydrol (30%).

Ethyl Alcohol (95%).

Diethyl Ether (anhydrous). The ether should be free of alcohol, and 1 ml. of water should dissolve in 150 ml. of ether at room temperature to give a clear solution.

Acetone. Free of aldehydes.

Distilled Water.

Molybdate Solution. Fifty grams of ammonium sulfate is placed in a 1-liter volumetric flask and dissolved in 500 ml. of concentrated nitric acid (sp. gr.: 1.36); 150 g. of powdered ammonium molybdate is dissolved in 400 ml. of boiling distilled water, cooled to room temperature, and poured slowly, with constant stirring, into the ammonium sulfate-nitric acid solution. The flask is then filled up to the mark with distilled water, allowed to stand for three days, and filtered through an ordinary filter into a glass-stoppered brown reagent bottle; it is kept in a dark, cool place.

Nitric-Sulfuric Acid Mixture. Thirty milliliters of concentrated sulfuric acid (sp. gr.: 1.84) is poured into 1 liter of nitric acid (sp. gr.: 1.19–1.21), which is obtained by mixing 420 ml. of nitric acid (sp. gr.: 1.40) with 580 ml. of distilled water.

Aqueous Solution of Ammonium Nitrate (2%). The solution should be slightly acidic; 1 or 2 drops of nitric acid may be added if necessary.

Fusion Mixtures:

(a) Potassium hydroxide and potassium nitrate (5 : 1).

(b) Potassium nitrate and sucrose (3 : 1).

Procedure

*Wet Combustion.*¹⁰ The substance is weighed in the weighing tube and transferred to a clean and dry Kjeldahl digestion flask; 0.5 ml. of concentrated sulfuric acid and 0.5 ml. of perhydrol are added to the

sample and the mixture is heated over the flame of a microburner, or in series determinations, on the digestion oven until fumes of sulfur trioxide begin to appear. This procedure is repeated at least twice with the addition of a few drops of perhydrol each time. Concentrated nitric acid may be substituted for the perhydrol if the substance appears not to be oxidizable with the concentrated sulfuric acid-perhydrol mixture alone (fats, etc.). When the digestion mixture is clear, it is allowed to cool and then it is diluted with 1 to 2 ml. of distilled water. The resulting solution is rinsed into the precipitation tube, 1 to 2 ml. of distilled water being used for each rinsing. Nitric-sulfuric acid mixture is added to the solution in the precipitation tube to bring the total volume to 15 ml.

(a) *In the Silver Crucible.*² The substance is weighed in the weighing tube and transferred to the crucible. Approximately 1.2 g. of potassium nitrate-potassium hydroxide mixture is added to the sample and the mixture is fused by heating the upper part of the crucible with a small non-luminous flame while the crucible is rotated and then slowly lowered into the flame. In about three minutes the fusion is complete, as shown by the clearness of the melt. The crucible is covered and allowed to cool by standing on a metal block for four or five minutes. Slight pressure on the walls of the crucible will loosen the melt, which is then transferred to the precipitation tube. The crucible is washed three or four times with about 2 ml. of distilled water, and the washings are also collected in the precipitation tube. Enough of the nitric-sulfuric acid mixture is added to the solution to bring the volume up to 15 ml.

(b) *In the Bomb.*³ The substance is fused in the bomb as described in the respective bomb method for the determination of halogen (p. 165). After the bomb is cool, the melt is dissolved in as small a volume of distilled water as possible. During the cooling, and with caution, 5 ml. of the nitric-sulfuric acid mixture is slowly added. The mixture is then quantitatively transferred to the precipitation tube; it must be filtered if cloudy or turbid. Enough of the nitric-sulfuric acid mixture is added to bring the total volume of the solution to 15 ml.

Precipitation.^{9, 13a, 14} The precipitation tube containing the reaction mixture, as obtained in any of the three oxidation methods given above, is heated on the steam bath for ten minutes. Then 15 ml. of the freshly filtered molybdate reagent is run into it from a pipet without touching the wall of the precipitation tube. After two to three minutes the mixture is shaken thoroughly and allowed to stand for at least six hours. Very small amounts of phosphorus require a considerably longer time, e.g., 0.5 mg. of phosphorus up to eighteen hours, and less than 0.5 mg. up to thirty-six hours.

Filtration. The filter tube is prepared before being weighed by placing it on the filtration apparatus and washing it with water, hot dilute nitric acid, and distilled water; the last traces of distilled water are removed by rinsing the filter tube twice with alcohol and twice with acetone and finally with ether. The filter tube is wiped with a moist flannel and dry chamois and placed in a desiccator, which is evacuated on the water pump; no drying agents are used in the desiccator. The filter tube is removed from the desiccator thirty minutes later and weighed five minutes afterwards. The ammonium phosphomolybdate precipitate is transferred to the filter tube by means of the same filtration arrangement as is used for the filtration of the silver halide (p. 152). After the supernatant liquid has been siphoned off, the precipitate is washed thoroughly with 2% ammonium nitrate solution and transferred to the filter tube. To remove the last traces of precipitate from the wall of the precipitation tube, it is rinsed alternately with the 2% ammonium nitrate solution and 95% ethyl alcohol. The filter tube is washed twice with alcohol, then with acetone, and finally with ether. After wiping, the filter tube is placed in the desiccator, which is evacuated. It is left in the desiccator for thirty minutes, and five minutes after its removal it is weighed to ± 20 micrograms.

Time:

| | <i>Minutes</i> |
|--|----------------|
| Weighing of the sample..... | 10 |
| Digestion or fusion..... | 30 |
| Precipitation *..... | 15 |
| Washing and drying of the filter tube..... | 40 |
| Weighing of the filter tube..... | 10 |
| Filtration..... | 15 |
| Drying of the filter tube..... | 30 |
| Weighing of the precipitate..... | 10 |
| Total..... | <hr/> 160 |

Calculation:

Log of weight of precipitate,
 Plus log of factor (16209),
 Plus negative log of weight of sample;
 Antilog of total = percentage phosphorus.

* The waiting time necessary for complete precipitation is not included in this time schedule.

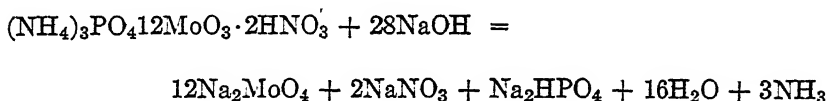
Remarks

In addition to the *wet combustion* method for the determination of phosphorus in organic compounds, as devised by H. Lieb and O. Winter-

steiner,¹⁰ and the two *fusion* methods, as devised by A. Elek² and A. Elek and D. W. Hill,³ other fusion methods are known^{1, 9, 13a, 14} which have been used with varying success.

The phosphorus in organic compounds may also be determined *volumetrically*.^{5, 6, 8} The organic substance is decomposed either by fusion or wet combustion, and the precipitation is carried out in a 100-ml. beaker. After standing over night, the supernatant liquid is filtered through a hard filter; then the precipitate is washed with 4 to 5 ml. ice-cold 50% alcohol and rinsed from the filter back into the beaker. The precipitate is dissolved in 0.1 *N* alkali, twice as much as will just dissolve it being taken. The ammonia is driven off by boiling the solution for at least thirty minutes. Two or three drops of 1% phenolphthalein indicator solution and an excess of about 4 ml. of 0.1 *N* acid are added to the alkaline solution, after which the solution is boiled for approximately fifteen seconds, then cooled and titrated back with 0.1 *N* sodium hydroxide solution to the usual end point.

The reaction involved in the titration of the ammonium phosphomolybdate is as follows:⁷



The phosphoric acid, as produced in the wet combustion or in fusion procedures, may also be *precipitated* as *strychnine phosphomolybdate*.⁴ The ratio of phosphorus to strychnine phosphomolybdate is 1 : 89. Since the precipitation is quantitative even in the cold, it can be filtered after thirty minutes. If the organic substance also contains arsenic acid it is removed before precipitation by distilling off the arsenic trichloride in a slow stream of hydrogen chloride. According to whether the phosphorus is determined gravimetrically or nephelometrically, the oxidation mixture is evaporated down with nitric acid or hydrochloric acid, respectively.⁸

A *Drop-Scale* procedure for the determination of phosphorus has been described by R. Lindner and P. L. Kirk.¹¹ The method is based on the acidimetric titration of the ammonium phosphomolybdate. The quantities of phosphorus determined ranged from 0.5 to 9 micrograms.

Other methods for the determination of phosphorus in organic compounds involve *colorimetric* methods,¹⁷ the *measuring* of the ammonium phosphomolybdate *precipitate* ($\pm 5\%$),¹⁶ and determination as *magnesium pyrophosphate*.¹⁵

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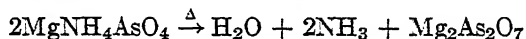
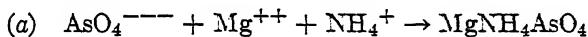
IX. OTHER ELEMENTS

Existing micromethods for the quantitative determination of metals and non-metals in both inorganic and organic compounds have been extensively reviewed by A. A. Benedetti-Pichler (metals, 130 papers; ^{4a} non-metals, ¹⁵⁷ papers ^{4b}) and by C. J. van Nieuwenburg.²²

In the following an account is given of micromethods for the quantitative determination of elements which are of lesser importance in quantitative organic elementary analysis than those presented in the preceding chapters.

Arsenic

The organic substance containing arsenic is oxidized similarly to compounds containing phosphorus. Either *wet combustion* ^{15, 16, 20, 23a, 25a, 38} (Carius method, see p. 151), or *Kjeldahl digestion* method, p. 200, or *fusion* ³ (bomb method, p. 201) is employed. The arsenic acid formed is determined either (a) *gravimetrically* as magnesium pyroarsenate, or (b) *iodometrically* ^{14, 35} as follows:



The following reagents are necessary: concentrated sulfuric acid (sp. gr.: 1.82), concentrated nitric acid (sp. gr.: 1.42), concentrated hydrochloric acid (sp. gr.: 1.19), perhydrol, magnesia reagent (5.5 grams magnesium chloride and 10.5 grams ammonium chloride dissolved in 100 ml. of distilled water), ammonium hydroxide solution (2 N), sodium peroxide, potassium iodide.

Precipitation and Filtration. The oxidation mixture, as obtained in the wet combustion or fusion method, is rinsed into a Pyrex glass evaporating dish and then is evaporated to dryness on a steam bath. The residue is dissolved in 3 to 4 ml. of 2 N ammonium hydroxide solution, and 1 ml. of magnesia reagent is added. The precipitate is amorphous at first, and to permit it to become crystalline it is left standing for at least six hours. The magnesium ammonium arsenate is transferred to a Neubauer platinum crucible with the aid of a feather

and is filtered as described in the corresponding determination of sulfur (p. 194). The last traces of precipitate are transferred from the glass dish to the crucible by rinsing the dish alternately with 2 *N* ammonium hydroxide solution and ethyl alcohol. After all liquid has been filtered off, the precipitate in the crucible is washed with 3 ml. of 2 *N* ammonium hydroxide solution. Then the crucible is removed from the filtration apparatus, closed with the lid and lower cap, and strongly ignited on a platinum cover. The magnesium pyroarsenate still contains traces of magnesium salts at this point and, therefore, must be washed again with dilute ammonium hydroxide solution. After the crucible has been re-ignited it is placed on the metal block of the microdesiccator and is weighed after ten minutes. An accuracy of $\pm 0.2\%$ is claimed for this method.

Titration. The oxidation mixture, as obtained in the Kjeldahl digestion process or by the bomb method, is rinsed with distilled water into a ground-glass-stoppered 125-ml. Erlenmeyer flask and heated to boiling for a few seconds. Two milliliters of 4% potassium iodide solution is added to the arsenic solution in the Erlenmeyer flask which is stoppered and the mixture is allowed to stand for ten minutes. The liberated iodine is then titrated with 0.01 *N* sodium thiosulfate solution. When the solution is faintly yellow, the liquid is diluted to about 20 ml. with freshly distilled water, 4 or 5 drops of starch indicator solution are added, and the titration is completed. A faint reddish tint is considered to be the end point. It is usually necessary to correct for a blank, but such a correction should not exceed 0.3 ml. of the 0.01 *N* sodium thiosulfate solution.

Calculation:

Gravimetric:

Log of weight of precipitate,
Plus log of factor (68368),
Plus negative log of weight of sample;
Antilog of total = percentage arsenic.

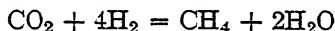
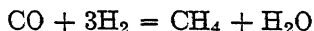
Iodometric:

Log of ml. 0.01 *N* sodium thiosulfate solution,
Plus log of factor (57380),
Plus negative log of weight of sample;
Antilog of total = percentage arsenic.

and the resulting oxidation mixture is subjected to *electrolysis*, by using plain platinum electrodes for copper and gold-plated platinum electrodes for mercury, in the electrolysis apparatus of F. Pregl,^{23b, 25b} which recently has been improved by A. Llacer, J. A. Sozzi, and A. A. Benedetti-Pichler.¹⁸ **Mercury** may also be determined gravimetrically²¹ after the organic mercury compound has been subjected to dry combustion and then the liberated mercury absorbed in a suitably constructed absorption tube containing gold leaf.

Oxygen

Of the several methods for the direct determination of oxygen in organic compounds the semi-micro method of H. Ter Meulen and J. Heslinga,³⁰ which has been repeatedly modified for micro work, appears thus far to have found the widest application.^{1, 8, 9, 11a, 13, 17, 26, 32, 33} The method involves destructive hydrogenation of the organic substance with gravimetric or titrimetric^{13, 17} determination of the water formed. The reactions involved are as follows:



Thus, for each oxygen atom present in the compound, one mole of water is formed.

Of the micromethods, the procedure devised by J. Unterzaucher and K. Bürger,³³ which follows rather closely the apparative arrangement and procedure of the regular carbon and hydrogen method (p. 101), appears to be the simplest. The apparatus consists of a hydrogen tank, followed by a drying tube filled with phosphorus pentoxide, a Friedrich-type pressure regulator (p. 134), a preheater containing a copper spiral; another drying tube follows, which in turn is attached to the hydrogenation tube—a regular side-arm combustion tube. The hydrogenation tube contains silver wool, the *cracking* agent (platinized powdered quartz), calcium oxide, a nickel spiral, and the *hydrogenation catalyst*, which consists of a mixture of activated nickel (prepared from nickel formate), thorium oxide, and powdered quartz. A Blumer-type vertical absorption tube (p. 137), with ground-glass joints and filled with phosphorus pentoxide, is used for the absorption of water. The customary Mariotte flask terminates the apparative arrangement. The combustion and sweeping-out process requires 100 ml. of hydrogen at a speed of 10 ml. per minute. The total time for one determination, including the wiping and weighing of the absorption tube, is about fifty minutes.

Other methods involve gasometric determination of the residual oxygen after complete dry combustion of the substance,¹¹ pyrolysis of the substance in an atmosphere of nitrogen,^{27, 40} and various wet combustion methods^{5, 7, 28, 29, 36, 37} involving "organic oxidation equivalent analysis"^{5, 36, 37} and the determination of "oxygen values."²⁸

Selenium in organic compounds may be determined *gravimetrically*. A suitable micro procedure, based upon the earlier methods of F. Wrede³⁹ and of H. D. K. Drew and C. R. Porter,⁶ has been devised by H. K. Alber and J. Harand² and S. Umezawa.³¹ The organic compound is combusted catalytically in an atmosphere of oxygen in a spiral combustion tube as in the respective catalytic combustion method for halogen (p. 160). The selenious acid thus formed is reduced to elementary selenium by means of sulfur dioxide in hydrochloric acid solution, and the precipitated selenium is filtered with the usual halogen filter tube (p. 152), which may be provided with a suitable cap.

Very small amounts of silver may be determined *photometrically*¹² as silver dichromate.

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DETERMINATION OF MOLECULAR WEIGHT

I. EBULLIOSCOPIC METHODS

Principle

The elevation of the boiling point of a known, pure organic solvent, caused by a known amount of a solute (the sample) with which it must not react, is determined by means of a suitably constructed Beckmann thermometer. The various apparatus are designed so that the determination may be carried out with small amounts of material—1.5 to 5 ml. of solvent and from 10 to 25 mg. of solute. Proper apparatus arrangement is provided to ensure maximum constancy of temperature.

Apparatus

Pregl's Apparatus (Fig. 48, *a*, *b*).^{3, 6a} This consists of a stand to hold the microburner (*a*) and a round metal plate (*b*) 9 cm. in diameter, provided with concentric rings for the support of three concentric glass cylinders (c_1 , c_2 , and c_3) which surround the boiling chamber (*d*) of the apparatus. The dimensions of the cylinders, which serve to provide an evenly heated and well-circulated air current, thereby ensuring maximum constancy of temperature, are as follows: c_1 , the outer cylinder, is 14 cm. high and 8.4 cm. in diameter; the middle cylinder, c_2 is 12 cm. high and 4.8 cm. in diameter; the innermost cylinder, c_3 , has a constriction in the middle, is 11 cm. high, 2.6 cm. in diameter at the top, and 3.6 cm. in diameter at the base. The chamber which extends into the neck of cylinder c_3 is 6 cm. high, 1.8 cm. in diameter, and contains the solvent, the solute, and the platinum tetrahedrons. Cylinder c_4 , which serves the purpose of diverting the air current rising from the microburner, is 2.6 cm. high and 3.6 cm. in diameter and is made of mica or any heat-resistant transparent material. Its top has an opening just wide enough to permit the insertion of the boiling chamber. The cylinder is held in place by three narrow strips of asbestos paper which are inserted between it and cylinder c_3 . The vessel carries two long side arms, one 10 cm. in length, with a ground-glass cap for the insertion of the sample, and a second one 13 cm. in length, serving as a

reflux condenser. A Beckmann thermometer, with a range of 3° , divided into 0.01° , is inserted into the neck of the boiling chamber by means of a tightly fitting cork. The apparatus is supported by two horizontal clamps fastened to the adjustable vertical column of the stand and has a suitably perforated celluloid shield for protection against

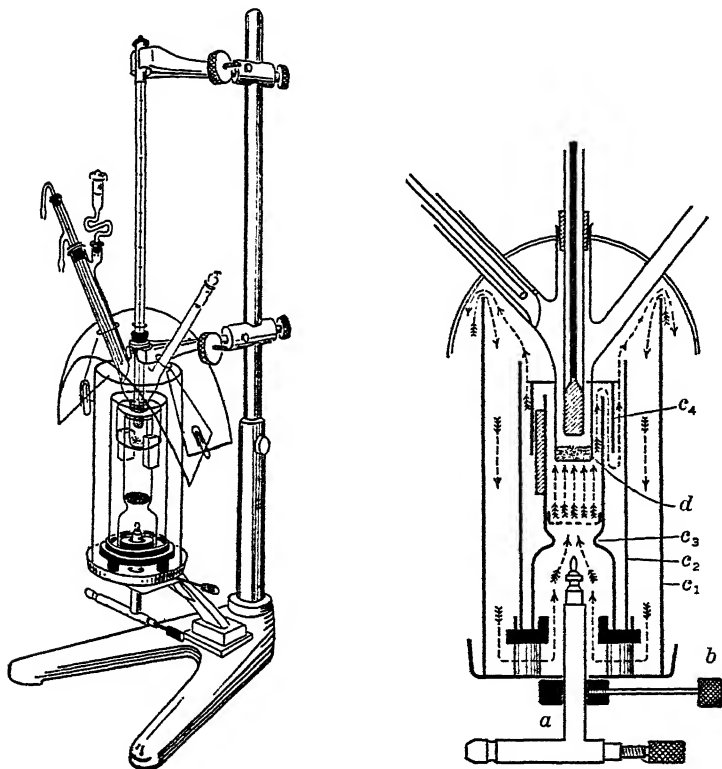


FIG. 48. *a*, Pregl Molecular-Weight Apparatus, Assembled; *b*, Diagram. Explanation in Text.

drafts from above. Platinum tetrahedrons are introduced into the chamber (*d*) to prevent superheating.

Rieche's Apparatus (Fig. 49, *a* and *b*).⁵ This apparatus has only one side arm (*a*), which serves as a reflux condenser as well as for the introduction of the sample through a vertical opening (*b*). To prevent superheating and to ensure a maximum constancy of temperature, so vital in this determination, the apparative arrangement is such that the micro

Beckmann thermometer, which is identical with the one used in the Pregl apparatus, is surrounded by the boiling solution and also by the vapor of the solvent. Newer modifications ensure this to a still higher degree.^{5a} A side arm (c) is attached to the boiling chamber (d) to provide for the necessary circulation of the boiling liquid. Platinum tetrahedrons (0.3 gram) are introduced into the bulb to minimize superheating of the reaction mixture.

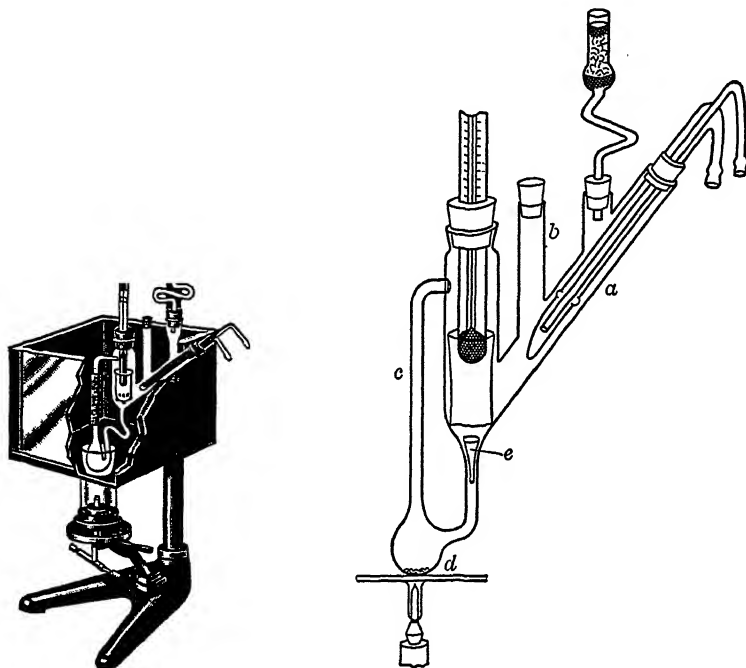


FIG. 49. a, Rieche Molecular-Weight Apparatus; b, Diagram.
Explanation in Text.

Sucharda-Bohranski-Schmitt Apparatus (Fig. 50).^{7, 9} The assembled two-piece apparatus has an overall length of 12.5 cm. and is 25.5 cm. high. It consists of: (a) the pear-shaped boiling chamber, which is 3.5 cm. high and 1.7 cm. in widest diameter, with fused-in glass splinters to ensure even boiling; (b) an undulating tube of 9-cm. length and 5-mm. diameter; two thermometer cups (c and d) of which the inner (c) is 2 cm. in diameter and 4 cm. in height and the outer (d) is 2.5 cm. in diameter and 6.5 cm. in height which is provided with a receptacle (e) 4.5 cm. deep for the insertion of the micro Beckmann thermometer;

(f) the reflux condenser, the base of which is connected with the thermometer cups by a straight siphon tube (g) 8.5 cm. long and 8 mm. in diameter. The condenser is also connected with the boiling chamber by means of a suitably constructed overflow tube (h), which is 3 mm. in diameter. The condenser is 18 to 20 cm. long, has an inside diameter of 1 cm., and is provided with a water jacket and a standard ground-glass joint.

Precision Pipets (1.5, 4.0 and 5.0 ml.).

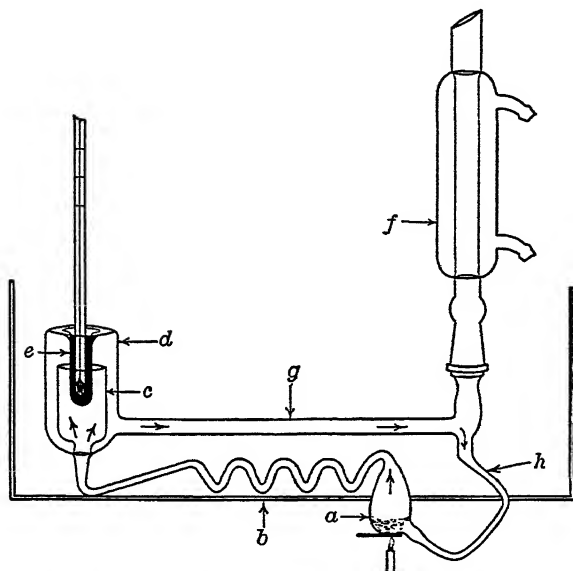


FIG. 50. Sucharda-Bobranski-Schmitt Apparatus. Explanation in Text.

Solvents

Only solvents of highest purity can be used. The usual solvents for these determinations are: acetone, absolute ethyl alcohol, ether, benzene, glacial acetic acid, chloroform, or water.

Procedure

PREPARATION OF THE SAMPLE

Solids. It is advisable to use the sample in the form of a pellet, which is prepared with the aid of the pellet press. About 10 mg. is used for the Pregl apparatus and 15 to 25 mg. for a determination with the Rieche or Sucharda-Bobranski-Schmitt apparatus. The sample,

pressed into a single pellet, is weighed in a weighing tube and need not be weighed more accurately than to ± 0.01 mg.

Liquids. Weighing pipets or capillaries as used in the vaporimetric molecular weight determination (p. 46) are employed.^{6b}

PREPARATION OF THE APPARATUS

Pregl^{3, 6a} and *Rieche*⁵ Apparatus. The platinum tetrahedrons are first introduced into the boiling chamber, the Beckmann thermometer is inserted, and the reflux condenser is attached. The solvent, 1.5 ml. for the Pregl apparatus and 4 ml. for the Rieche apparatus, is measured accurately with a precision pipet and is introduced next. The apparatus is slowly heated by means of a microburner; careful regulation of the flame is absolutely essential for the success of the determination. The Beckmann thermometer, previously adjusted to the boiling-point temperature of the solvent, is read to 0.002° with the aid of a magnifying lens, and as soon as two consecutive readings, taken at an interval of two to three minutes, are identical (T_1), the sample is added through the side arm. No changes in the procedure of heating are made during this operation and the subsequent observations. Ten minutes later the Beckmann thermometer is again read, and the end point is reached when two consecutive readings, taken at a time interval of several minutes, are the same (T_2). If necessary, the sample may be recovered after the determination by transferring the reaction mixture to an evaporating dish and evaporating the solvent.

Sucharda-Bobranski-Schmitt Apparatus.^{7, 9} About 5 ml. of solvent and 18 mg. of solute are necessary for one determination. Approximately 3 to 4 ml. of mercury is required to surround the mercury bulb of the Beckmann thermometer, which is inserted in the outer cup and held by a clamp. Under the boiling chamber there should be an asbestos wire gauze and a microburner provided with a chimney. An asbestos board is placed under the apparatus, and when low-boiling solvents, such as acetone, are used, it is necessary to surround the entire apparatus with asbestos board.

These precautions are necessary in order to be able to regulate the heating of the boiling liquid to constant temperature and also to avoid superheating of the solvent. The flame of the microburner is regulated so that the liquid gently overflows the rim of the inner cup. Occasionally it may be necessary to heat the outside of the cup with a small flame of a gas burner, especially when a large amount of solvent accumulates at the bottom of the cup and thereby prevents free circulation of the liquid. This may occur at the beginning of the experi-

ment. Five to seven minutes after regular circulation of the boiling solution has been established, the temperature readings should not vary, more than $\pm 0.002^{\circ}\text{C}$. When this constancy of temperature has been reached, then the boiling point of the solvent is recorded; the microburner is removed for five minutes, and the sample is added to the solvent. If the sample is added in the form of pellets, it may be added through the condenser; however, if the sample consists of small crystals or is in form of a powder, then the condenser is removed and the sample is added directly to the solvent. Some substances cannot be pressed into pellets and hence the ground-glass joint at the base of the condenser is of advantage.

After the introduction of the substance the microburner is again placed under the boiling chamber; the sample is dissolved in the solvent, which is heated continuously until the boiling liquid circulates freely through the apparatus. Three to five minutes later the elevation of the boiling point of the solvent is read to within $\pm 0.002^{\circ}\text{C}$., and when constancy of temperature has been obtained, as ascertained by a second reading several minutes later, the determination is completed.

It is very important that the entire apparatus be shielded from drafts or currents of air; unless this precaution is observed accurate results cannot be obtained, which is particularly true of low-boiling solvents; with benzene and such solvents having a higher boiling point there is less danger of inaccuracy.

Calculation:

Log of molecular boiling-point elevation constant (see p. 299).
Plus log of weight of sample,
Plus negative log of weight of solvent,
Plus negative log of observed elevation of boiling point;
Antilog of total = molecular weight.

Remarks

For all three methods presented in this manual, both good^{3, 6a, 7, 9} and unsatisfactory results have been claimed.^{1, 8} At present the Sucharda-Bobranski ebullioscopic method,⁹ which was improved by R. B. Schmitt,⁷ seems to be more widely used than either the Pregl^{3, 6a} or the Rieche method.^{1, 5}

Aside from modifications of the Pregl ebullioscopic method,⁴ a new micro ebullioscopic molecular-weight determination method, based upon the corresponding macromethod of A. W. C. Menzies and S. L. Wright,² has been developed by J. H. C. Smith and H. W. Milner.⁸

In these methods great difficulty is experienced in maintaining an *absolutely* constant temperature. Most of the time the temperature

continues to rise slowly and constantly. It is therefore recommended that not only the boiling points but also the time of observation be recorded. Then, in determining the rise in the boiling point (Δ), only the boiling points recorded after the same time interval should be compared, i.e., the boiling point of the solvent obtained after ten minutes is compared with the boiling point of the solvent and solute after ten minutes, etc. Another way to overcome this general difficulty is to use two apparatus, one with the pure solvent and one with the solution, and observe the respective boiling points at ten, fifteen, twenty, and thirty minutes. The increments at equal elapses of time are then averaged for the final calculation.

The molecular weight of an unknown or a new compound should be determined with at least two different solvents and, if possible, should be checked by either the cryoscopic, the vaporimetric, or the isothermic method.

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II. CRYOSCOPIC METHOD

Principle

The substance to be analyzed is dissolved in a suitable solid organic solvent, and the resulting depression of the melting point of the solvent is observed.⁹⁻¹¹ Essential requirements are ease of crystallization of the solvent and solubility of the solute in the solvent; furthermore, the solute must not react with the solvent, nor should it decompose at the temperature of the melting point of the solvent. By using solvents with a very high molecular melting-point depression constant,⁵ such as camphor or borneol,^{6, 8} the technic involved is reduced to elementary simplicity and involves merely the taking of a melting point in the conventional manner with the necessary precautions against superheating and changes in the concentration of the reaction mixture.

Apparatus

An ordinary melting-point apparatus, with the exception of the Thiele apparatus, can be used, although a Fisher melting-point apparatus³ is preferable. An Anschütz thermometer with the proper temperature range (100° to 180° for camphor, or 150° to 220° for borneol) and subdivided into 0.2°, is most suitable. Concentrated sulfuric acid, dibutylphthalate, or Crisco is employed as the bath liquid.

Solvents

Camphor is most commonly used as a solvent. It should be of the highest purity, and it is advisable to resublime it. It is kept in a well-stoppered wide-mouth reagent bottle. Its melting point, as well as the molecular melting-point depression constant, should be redetermined for every fresh batch of camphor by using a known and pure solute, such as azobenzene or naphthalene. These constants may vary, depending on whether the camphor employed is natural or made synthetically, and wide variations have been reported in the literature. The same holds true for borneol,⁸ which may also be used in this type of molecular-weight determination.

Procedure

Solids. A thin-walled conical capillary, of the dimensions given in Fig. 51, is sealed in such a way that a thick bottom is avoided. This capillary (*a*) is wiped with a chamois and weighed after several minutes.

It is most conveniently handled with the chamois-tipped capillary forceps, or with the chamois finger cots. Then about 1 mg. of substance is introduced and the capillary is weighed again. The substance is introduced as follows: The sample is placed on a small watch glass and taken up with another capillary (*b*), which fits into (*a*) and has a fire-polished orifice. Capillary (*b*) is wiped clean on the outside and then it is placed sufficiently far down into (*a*) to effect a clean introduction when the substance is pushed out with a thin, fire-polished glass rod. It is obvious that serious errors would result if some of the substance were scattered all along the side wall of capillary (*a*), where it could not be mixed with the solvent. Next, an amount of solvent, which, depending upon the molecular weight of the substance, should be 10 to 20 times the

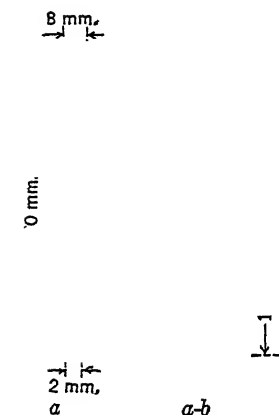


FIG. 51. *a*, Conical Capillary; *a-b*, Capillary *b* Inserted into *a* for the Introduction of the Solvent or Substance; *c*, Capillary *a* Sealed; *d*, Solvent and Substance Molten in Capillary *a*.

amount of sample used, is introduced in the same manner, but with another and somewhat wider capillary. Capillary (*a*) is then weighed again, the weight of the solvent being thus obtained.

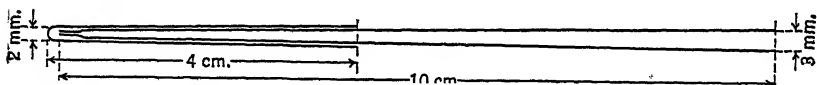


FIG. 52. Pipet for the Introduction of Liquids into the Conical Capillary.

Liquids.^{9, 11, 12} Liquids are introduced into the conical capillary with the aid of a suitable pipet shown in Fig. 52, with adequate precaution against losses of the liquid solute due to evaporation, adhesion to the walls of capillary (*a*), etc. In many cases it is advisable to intro-

duce the solid solvent first and to add the liquid solute after the weight of the solid solvent has been determined.

Heating. After the weight of capillary (*a*), together with that of the solute and the solvent, has been determined, it is sealed as follows: The capillary is held into the non-luminous flame of a microburner 1 to 1.5 cm. above the camphor and heated, while being rotated, until the wall of the capillary collapses to a solid glass rod, which after it is removed from the flame, is drawn out as shown in Fig. 51c. The capillary is then attached to a thermometer calibrated to 0.02° , so that the bottom of the capillary is flush with the end of the thermometer and both are immersed deeply enough in the heating bath of the melting-point apparatus so that the sealed end of the capillary is about 1 cm. below the level of the bath liquid. The bath liquid is heated by means of a microburner to the melting point of camphor, then allowed to cool to the freezing point of the solute-solvent mixture, after which the heating is repeated; this is usually sufficient to mix the solvent thoroughly with the sample. The mixture is again permitted to cool and then it is heated very slowly, at a rate of 0.5° per minute, and the melting point is noted when the last crystal disappears, which happens shortly after the lattice of the crystals collapses and sinks to the bottom of the capillary. The cooling and melting are repeated until a check in temperature of $\pm 0.2^\circ$ is obtained. The melting point of the solvent is taken at the same time and under the same conditions by attaching a similar capillary containing only camphor to the thermometer; in this manner stem corrections, as well as possible errors due to inaccuracies of the thermometer, are avoided. With some substances the freezing point of the solute-solvent mixture is more readily observable than the melting point, owing to a better visibility of the onset of crystallization, in which case, of course, the freezing point of camphor is also determined under identical conditions. The calculation, whether the freezing point of camphor or the depression of the freezing point is used, remains the same.

Calculation: ⁶

Log of molecular melting-point depression constant (see p. 299),
Plus log of weight of sample,
Plus negative log of weight of solvent,
Plus negative log of observed depression of melting point or freezing point;
Antilog of total = molecular weight.

Remarks

It is often advisable to observe the melting point as well as the freezing point of the mixture and the pure solvent; then T_1 and T_2

must be either melting points or congealing points, respectively. Of the many modifications suggested,^{1, 2, 4, 7, 8, 13} the methods employing sealed capillaries have been found superior, because concentration changes due to sublimation of the solvent are largely eliminated.

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III. VAPORIMETRIC METHOD

Principle

The principle involved in this method is the vaporization of the organic substance in a closed system in such a manner that its vapors displace an equal volume of mercury under controlled conditions.²¹ The displaced mercury is determined gravimetrically. The necessary corrections for pressure, temperature, and expansion of the mercury and apparatus being applied, the volume of the vapors under standard conditions is determined and from this volume the vapor density or molecular weight of the substance is calculated. Two types of apparatus are used, one for low-boiling liquids and another for higher-boiling liquids or for solid substances.

Apparatus

For Low-Boiling Substances (Fig. 53). This apparatus is employed for liquids boiling below 100° C., and consists of a flask (*a*) of about 100-ml. capacity. A tube (*b*), 10 cm. long and of 5- to 7-mm. bore, sealed to the upper part of the flask, serves as the receptacle for the thermometer (*c*). A side arm (*f*) of 3-mm. bore is connected to the bottom of the flask by a ground-glass joint (*e*); it is long enough to extend 1 to 2 cm. above the surface of the bath and then is bent horizontally for a length of about 6 cm. The arrangement of the flask in the heating bath (*g*) and the position of the receiver for the mercury (*h*) are shown in the illustration.

For High-Boiling Substances (Fig. 54). This apparatus is used for liquids or solids boiling up to 330° C.; it consists of a round-bottomed 350-ml. Pyrex flask (*a*), which serves as the container for the bath liquid. The neck is sealed tangent to the surface of the flask and is 7 to 8 cm. long, with an inner diameter of about 2 cm. By means of an interchangeable ground-glass joint (No. 15) either a Liebig water condenser or a plain air condenser (*b*) of 50-cm. length and with a large enough inner diameter (10 to 12 mm.) to permit the insertion of a thermometer (*c*) is connected to the flask. The Pyrex glass vaporizer (*d*), a slightly elongated or egg-shaped bulb of 12- to 15-ml. capacity, has a stem (*e*) 11 cm. long and 6 mm. in inner diameter sealed to its bottom at an angle

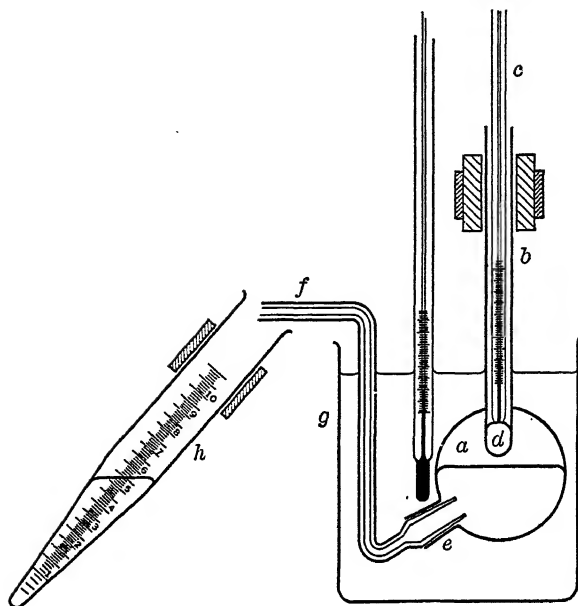


FIG. 53. Vaporimetric Molecular-Weight Apparatus for Low-Boiling Substances.
Explanation in Text.

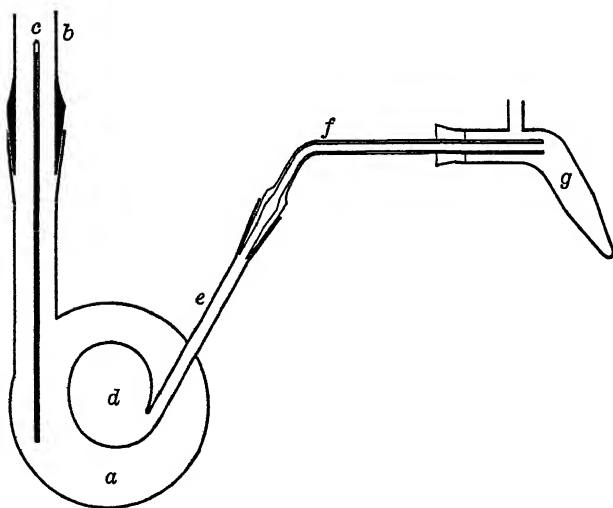


FIG. 54. Vaporimetric Molecular-Weight Apparatus for High-Boiling Substances.
Explanation in Text.

of 45 degrees. To facilitate the introduction of the capillary containing the sample, the inner diameter of the bend between the vaporizer and the stem must be about 1 mm. wider than the inner diameter of the rest of the stem. The capillary outlet tube (*f*) is bent at an angle of 135 degrees and has an outer diameter of 5 mm. and an inner diameter of 2 mm. Its horizontal arm is about 10 cm. long; its oblique arm together with the interchangeable ground-glass joint is 5 cm. long. Between this ground-glass joint and the bend are two glass hooks for the attachment of steel springs leading to similar glass hooks on the stem to prevent the loosening of this connection during the determination. The entire vaporizer is fused to the heating flask opposite its neck at an angle of about 45 degrees in such a manner that the glass bulb is in the center of the heating flask and the orifice of the ground-glass joint extends at least 5 cm. beyond the heating flask. The thermometer is introduced through the condenser into the bath liquid and is held in place by a flexible wire. A centrifuge tube of about 15-ml. capacity, which is bent downward at an angle of about 135 degrees below the side arm, serves as the receiver (*g*) for the displaced mercury. By means of a suitably bent wire this receiver is attached to the top hook of the weighing pan of the analytical balance when it is weighed.

Mercury. The mercury used as the sealing liquid must be free from volatile substances. Of the many purification procedures the following appears to be entirely adequate. The mercury (commercial, c.p., or reclaimed) is first treated with concentrated sulfuric acid and then permitted to fall from a funnel, the stem of which is drawn out to a fine opening, in a fine stream into a 250-ml. graduate cylinder filled with dilute nitric acid (1 : 10). After this treatment it is placed in a strong separatory funnel and washed repeatedly with water, acetone, and finally with distilled water. Then the water is removed and the mercury placed in a thick-walled, round-bottom flask which is fitted with a capillary as in a distillation under reduced pressure. To remove the last traces of moisture the flask is then attached to a water suction pump and heated for 1 hour in an oil or sand bath at 250° C. Redistillation of the purified mercury may be substituted for the above procedure of heating.

Procedure

LOW-TEMPERATURE APPARATUS (Fig. 53)

Preparation of the Sample. The sample, which invariably is a liquid, is introduced by means of a capillary weighing pipet, as in the carbon and hydrogen determination, the introduction of potassium chlorate,^{24, 27} however, being omitted.

Heating. Since this apparatus is most practicable for liquids boiling below 100°C. , only liquid samples, introduced and weighed in capillary pipets as described above, need to be considered. The stem of such a capillary pipet is cut off just below the center bulb and the pipet is centrifuged to ensure against liquid remaining in the hair-fine ending. Then the pipet is cut about 1 mm. above the center bulb (see Fig. 55a), and the bulb containing the substance together with the hair-fine ending is placed in the vaporizer, which afterwards is filled with mercury up to the orifice of the ground-glass joint. The side arm is then attached and the entire capillary of the side arm is completely filled with mercury, as described for the high-temperature apparatus. The apparatus, with the receiver attached so that the side arm extends 2 to 3 cm. into the receiver, is placed in a beaker of water and allowed to reach equilibrium in temperature, that is, the thermometer in the water bath and the one in the top tube, which contains some mercury, have to register identical temperatures (T_1). Then the water in the beaker is heated with a gas burner to boiling, the heating being continued until the two thermometers again show the same temperature (T_2). The apparatus is cleaned and dried in the same manner as the high-temperature apparatus.

HIGH-TEMPERATURE APPARATUS (Fig. 54)

Preparation of the Sample

Solids. Capillaries (*b*, *c*) of not less than 1.5-mm. inner diameter are prepared by drawing out a soft-glass test tube in a Méker burner. These capillaries are cut to a length of about 8 cm., wiped with a chamois, placed on the hooks of the left-hand weighing pan of the balance, and weighed after several minutes. Such capillaries weigh about 150 mg. and are counterpoised either by another capillary or by the standard weights. The solid substance is melted on a microscope slide, on a watch glass, or in a capillary of wider bore. The weighed capillary (*b*) is brought in contact with the molten substance, which is allowed to rise in the capillary to a height of 3 to 4 mm.; this is equivalent to 5 to 8 mg. of substance. The capillary is then withdrawn and allowed to cool; if crystallization does not take place upon cooling, it is brought in contact with the remaining solid sample. After crystallization has set in, the outside of the capillary is wiped clean, placed on the hooks of the weighing pan of the balance, and weighed again. If the substance is a solid which does not melt, but sublimes, a melting-point capillary (*c*) of 2-mm. bore and sealed at one end is used. The weighed capillary, open at one or both ends, is cut about 2 mm. above the substance

(Fig. 55*b*, *c*), and the filled capillary, which should be short enough to pass the bend of the vaporizer, is introduced.

Liquids. Capillaries (*b*) open at both ends are used for liquids of high viscosity or syrups or semi-solids. Otherwise capillary pipets (*a*) are used. The stem of the capillary is cut off below the center bulb and the pipet is centrifuged to remove all liquid from its hair-fine end. Then it is cut above the center bulb as shown in Fig. 55*a*, and the bulb containing the substance is placed in the vaporizer. Special precautions are necessary when analyzing very volatile liquids; ice water is put in the flask previous to the introduction of the sample and the flask is stoppered. The mercury and the sealed capillary are cooled in a similar manner.

Filling the Apparatus. Clean and dry mercury is poured into the vaporizer already containing the sample, while the entire apparatus is held over a suitable trough. The filling is accomplished with a minimum of spilling by using a Kells-Ringer flask or similar device having double outlets, one of which has a fine opening. By proper tilting of

the flask, the entire bulb and the stem up to the ground-glass joint are easily filled with mercury. The joint of the capillary outlet tube is greased sparingly, and the tube is inserted into the stem of the vaporizer, the outlet tube being filled about one-third with mercury. The steel springs are then attached and the outlet tube is filled completely with mercury by means of a pipet, which is prepared by drawing out a soft-glass tubing to a fine enough capillary so that it fits about 2 cm. into the capillary outlet tube. This pipet is provided with a rubber cap, and by proper inflation a small amount of mercury is drawn into the pipet. The pipet is inserted into the capillary outlet tube and a small amount of mercury is introduced by applying pressure to the rubber cap. The column of mercury introduced in this manner is joined to the mercury column in the capillary outlet tube by inserting and withdrawing a fine copper or platinum wire. Finally, the weighed receiver is attached to the capillary outlet as shown in Fig. 54, and the entire apparatus is clamped to a suitable stand which is also provided with a ring clamp and wire gauze. Sufficient bath liquid to cover about two-thirds of the bulb of the vaporizer is introduced next; small pieces of porous tile are added to ensure even boiling, and the condenser is attached. A thermometer is

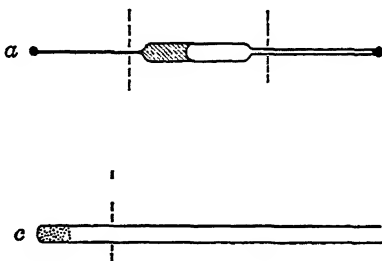


FIG. 55. Pipet and Capillaries for the Vaporimetric Molecular-Weight Determination. Explanation in Text.

inserted through the condenser into the bath liquid so that its mercury bulb is completely immersed. The apparatus is allowed to reach equilibrium of temperature, and then the starting temperature, T_1 , is noted. Any mercury which may have entered the receiver during this period is removed and the receiver re-attached.

Heating. After the starting temperature, T_1 , has been read, the apparatus is heated rather rapidly to near the boiling point of the bath liquid. The heating is carried out by applying a free flame, or using a suitable heating bath of oil, sand, or Wood's metal. As soon as the bath liquid begins to boil, the heating is reduced to a minimum and the boiling continued for exactly two minutes, at which time the thermometer inside the condenser is again read to give the end temperature T_2 . Then the heating is discontinued and the apparatus permitted to cool. The receiver containing the displaced mercury is removed and weighed on a macroanalytical balance to ± 0.1 gram.

Either apparatus can be easily refilled, if repetition of the determination is desired, by dipping the delivery tube into mercury before cooling. As the vapors in the vaporizer condense, the mercury will be drawn into the flask. This procedure permits a check determination without the introduction of a new sample. Furthermore, it is possible to determine both the boiling and the condensation point of the substance, namely, upon heating and upon cooling.

Cleaning the Apparatus. The bath liquid in the flask is poured into a suitable container and the flask stoppered. The capillary outlet tube is detached while the apparatus is held over a trough to collect any spilled mercury. The mercury from the vaporizer is emptied into a suitable bottle and at the same time the capillary from a previous determination is removed. About 2 ml. of acetone is introduced into the vaporizer, and the apparatus is well shaken, while its opening is stoppered with a suitable cork. The solvent is removed, and this operation is repeated three times. The apparatus is then placed in an oven heated to about 100°C. , and, while it is still warm, the outlet of the vaporizer is attached to a suction pump and evacuated.

Correction for Heat Expansion. By performing the experiment as described above with an empty capillary while the apparatus is heated from T_1 to T_2 , the amount of mercury expelled as the result of the expansion of the mercury and glass and of other factors, $c(T_2 - T_1)$, is determined. From the amount of mercury displaced at several temperature points—three are sufficient—a graph may be plotted and the amount of mercury collected from this particular apparatus ascertained for any temperature up to the boiling point of mercury.

Calculation:

Log of 62351 (79385),
Plus log of weight of sample,
Plus log of 373.2 (57194),
Plus negative log of pressure of vapor (see p. 300),¹⁸
Plus negative log of volume of vapor (see p. 300);
Antilog of total = molecular weight.

Remarks

The low-temperature apparatus (Fig. 53) has proved entirely satisfactory for temperatures up to 100° C.,^{21a, b} and so far no substance with a boiling point below this temperature has been encountered which did not give satisfactory results. Even very reactive substances such as alkyl chlorides, bromides, iodides, sulfides and acids, where possible interaction of the mercury with their vapors might be anticipated, gave normal values. At higher temperatures (200° C. and above) difficulties with the ground-glass joint at the bottom of the apparatus were experienced, and hence the form of the apparatus was changed by placing the ground-glass joint above the heating bath.^{21d, e} Further improvements were a fused-in thermometer with three graduations (100, 200, and 300° C.), but difficulties in obtaining constancy of temperature finally led to the construction of the high-boiling apparatus shown in Fig. 54.^{21c}

Although the vapors of the substance are not in contact with air, a fact which lessens the danger of possible oxidation, they are under higher (about 100 mm.) than atmospheric pressure. This pressure may be diminished by means of partial evacuation by attaching the side arm of the receiver to a suction pump with provision for the maintenance of a constant, although lower, pressure (about 300 mm.). The filling of the vaporizer may also be carried out by evacuation of the vaporizer containing the non-volatile sample and by suitable arrangement allowing the mercury to enter this portion of the apparatus. The boiling point as well as condensation point, which can be observed simultaneously while carrying out the determination, are comparable with the results obtained with other microboiling-point methods already known;^{1, 5, 9, 11, 14, 25-29, 31} corrections for the higher pressure (p_1 and p_2) are necessary, however. By slightly enlarging the bulb of the vaporizer without changing the apparatus otherwise, R. B. Schmitt³⁰ has shown that larger samples (10 to 20 mg.) can be used, which need only to be weighed to ± 0.05 mg., a precision obtainable with any ordinary analytical balance, thereby eliminating the use of a microanalytical balance. W. Saschek and F. Schneider²⁸ have

modified the apparatus so that the pressure of the vapors at constant volume is determined.

In the literature a number of microvaporimetric methods have been reported. Most of them are exact miniature editions of the corresponding macromethods. Thus the classical V. Meyer method¹⁹ served as a model for the corresponding micromethod of W. Nernst,²⁰ and later A. C. Bratton and H. L. Lochte⁷ demonstrated the applicability of this method to milligram samples of organic substances. Other micro-methods involve the basic principle of the method of A. W. Hofmann¹³ and the many modifications of both,^{2-4, 6, 8, 12, 15, 17, 18, 20, 22, 24} while E. W. Blank⁴ described a micro procedure based upon the classical Dumas method.^{10, 23}

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IV. ISOTHERMIC METHOD

Principle

This method of determining molecular weights is based upon isothermic distillation of volatile solvent from a solution of lower molarity to one of higher molarity. In a closed system this produces measurable changes in the volumes of such solutions. These volume changes are determined by following under a low-power microscope the changes in the position of the menisci of the two solutions contained in separate capillaries. By appropriately pairing standard solutions of various but known molarities with a solution of known concentration of a test substance in the same solvent and tabulating the ensuing changes in the volumes of the standard solutions, the molarity of the solution of the test substance is ascertained.

Apparatus

Microscope. An ordinary low-power microscope is used. (Objective 4.6x, ocular 7x.) The eyepiece carries a micrometer scale marked

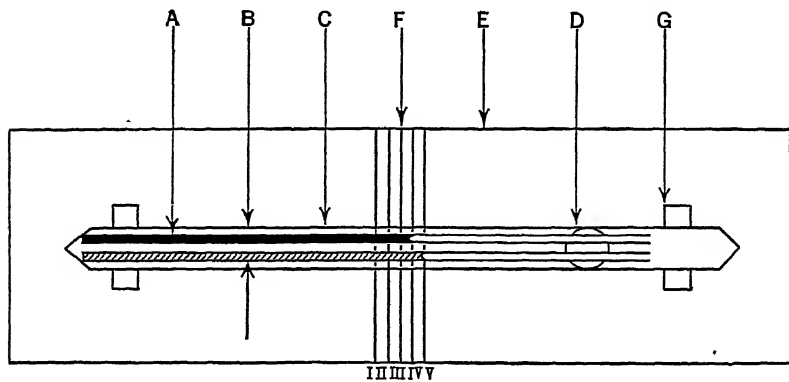


FIG. 56.

from 0 to 50. These 50 divisions correspond to 1.5 mm.; therefore 1 division corresponds to 0.03 mm.

Glass Plate (Fig. 56E). A rectangular glass plate about 12 cm. long, 4 cm. wide, and 2 mm. thick which possesses five parallel transverse

lines (*F*) situated near the center of the plate. The lines must not be more than 0.03 mm. thick and should be 3 mm. apart; they are appropriately marked (I, II, III, IV, V, etc.).

Capillaries. The capillaries are 10 to 12 cm. in length and about 1.5 mm. in inner diameter. They should be as uniform as possible, particularly in regard to the inner diameter (Fig. 56*A* and *B*).

Colored Glass Thread. Not more than 0.1 mm. in diameter.

Desiccator Tubes (Fig. 56*C*). These are ordinary glass tubings sealed at one end. They are 5 to 6 mm. in diameter and 15 cm. long.

Glass Wool (Fig. 56*D*). Pliable Pyrex glass wool is best, although ordinary cotton might be substituted.

Adhesive Tape (Fig. 56*C*). Ordinary surgical adhesive tape, 1 inch in diameter, is entirely satisfactory.

Volumetric Flasks with Ground-Glass Stoppers. Two 250-ml.; $\frac{1}{2}$ dozen 100-, 50-, and 10-ml.; 1 dozen 25-ml.; and 1 dozen 1-ml. (Similar to the tare bottles for the absorption tubes, p. 34.)

Pipets. One-milliliter capacity, calibrated in 0.1 ml.

Hand Centrifuge. Ordinary, as used in clinical analyses. Equipped with two metal tubes. The capillaries are inserted directly into these metal tubes.

Vacuum Pump. An ordinary tap-water aspirator pump producing a vacuum of 20–40 mm. is adequate.

Reagents

Solvents. Low-boiling solvents which can be used under atmospheric pressure (acetone, chloroform, etc.) are preferable, but higher-boiling solvents (ethyl alcohol, benzene, pyridine, dioxane, etc.) can also be used. Since the solvent for the standard and the sample must be the same, a sufficient amount should be available not only for the preparation of the standard but also for the various unknowns to be examined.

Standard Solutions. Ten standard solutions: 0.2, 0.15, 0.1375, 0.125, 0.1125, 0.1, 0.0875, 0.075, 0.0625, and 0.05 molar. These standard solutions are best prepared as follows:

First 250 ml. of 0.2 *M* solution is prepared by dissolving an appropriate standard sample, preferably a colored substance, accurately weighed on a macrobalance, in a solvent suitable for both the standard and the test sample (acetone, chloroform, ethyl alcohol, pyridine, etc.). Exactly one-half of this standard solution is transferred to another 250-ml. volumetric flask, using a 100-ml. and a 25-ml. volumetric flask for the transfer. These two flasks are then rinsed several times with the original solvent and these rinsings are added to the

solution followed by the addition of more solvent to bring the solution up to the mark. This then constitutes the 0.1 *M* standard solution. Twenty-five milliliters of the original 0.2 *M* solution is transferred into a 100-ml. volumetric flask and following the above rinsing and filling-up procedure, 100 ml. of the 0.05 *M* standard solution is obtained. Fifty milliliters of the same 0.2 *M* solution is transferred to another 100-ml. volumetric flask, but this time for the rinsing and the filling-up procedure portions of the 0.1 *M* solution are used to yield 100 ml. of the 0.15 *M* standard solution. Thus three more primary standard solutions (0.05, 0.1, and 0.15) are obtained.

The secondary standard solutions (0.0625, 0.075, 0.0875, 0.1125, 0.125, and 0.1375) are obtained by mixing equal quantities of the appropriate primary standard solutions, i.e.: 50 ml. of the 0.05 *M* solution is mixed with an equal amount of the 0.1 *M* solution to give 100 ml. of the 0.075 *M* standard solution. Twenty-five milliliters of this solution is again diluted with an equal amount of the 0.05 *M* primary standard solution to yield 50 ml. of the 0.0625 *M* standard solution; 25 ml. of the same 0.075 *M* solution is mixed with 25 ml. of the 0.1 *M* solution to form 50 ml. of the 0.0875 *M* standard solution. Fifty milliliters of the 0.15 *M* primary standard solution is introduced into a 100-ml. volumetric flask and, after rinsing of the 50-ml. transfer flask with portions of the 0.1 *M* solution and filling up the 100-ml. flask to the mark with portions of the same solution, 100 ml. of the 0.125 *M* standard solution is obtained. To prepare 50 ml. of the 0.1125 *M* solution, 25 ml. of the 0.1 *M* solution is mixed with an exactly equal amount of the 0.125 *M* solution, and finally 25 ml. of this solution is mixed with 25 ml. of the 0.15 *M* primary standard solution to yield 50 ml. of the 0.1375 *M* standard solution.

The ten standard solutions as prepared above are transferred and stored in properly labeled 25-ml. volumetric flasks.

Procedure

Preparation of the Sample Solution. The sample solution might be prepared on a macro (above 100 mg. substance), semi-micro (above 30 mg. substance), or micro scale. In the last case, 4 to 6 mg. of the sample is weighed in the weighing tube and transferred to a glass-stoppered tare bottle. This bottle with the substance is then weighed on an ordinary analytical balance within ± 1 mg. After the addition by means of a dropping pipet of approximately 0.5 ml. of the identical solvent as used for the standard solution, the bottle is weighed again while stoppered. The weight of the solvent thus found is divided by the specific gravity of the solvent to give the volume.

Preparation of Capillaries (Fig. 56A and B). One of the capillaries is filled to two-thirds its length (i.e., 8 cm.) with the solution of the unknown (B) by means of suction by mouth. For very volatile or mobile liquids it is advisable to have that end which dips into the solution drawn out to a hair-fine ending. That end of the capillary which is opposite the liquid is sealed in a microburner. After cooling, the solution is centrifuged toward this sealed end by means of a suitable hand centrifuge. No violent centrifuging is necessary, a single turn of the handle usually suffices. Three more capillaries are then filled, sealed, and centrifuged in exactly the same manner. Similarly the set of capillaries (A) containing the standard solutions (0.2, 0.15, 0.1, and 0.5 molar) is prepared. If the standard solution is colorless, each capillary is marked by inserting a small colored glass thread (0.1 mm. thick and 2 mm. long) into it before centrifuging. After this, each standard solution capillary is paired off with a capillary of the unknown, preferably in such a way that the menisci of the two solutions (0.05 to 0.08 ml.) are at approximately the same level.

Filling the Desiccator Tube (Fig. 56). Each pair (A and B) is then introduced, sealed end down, into the desiccator tube (C). Both capillaries should rest firmly at the bottom of the tube. A wad of pliable glass wool (D) is then introduced and pushed down into the tube to about 5 mm. below the openings of the capillaries, but well above the menisci of the solutions. The purpose of this wad is to keep the capillaries in the same position. The lower half of the tube thus prepared is immersed in a beaker containing ice water. After ten minutes the tubes are removed and dried with a towel; if a solvent boiling below 70° C. is used, the tubes are sealed off as close as possible to the open ending of the capillaries. If a higher-boiling solvent, b.p. > 70°, is used, the part above the capillaries is softened in a gas flame. The walls of the tube are allowed to collapse, and this portion of the tube is then drawn out into a capillary without breaking off the constriction thus produced. The tube is then put back into the ice water and allowed to cool and is afterwards evacuated to about 30–40 mm. pressure. An ordinary tap-water aspirator pump suffices for this purpose. While the tube is still attached to the aspirator pump, the capillary constriction produced previously is once more heated in the gas flame and allowed to collapse completely, thus forming a seal. The desiccator tubes thus prepared are then appropriately marked and placed in the beaker containing ice water.

Mounting of the Desiccator Tubes. After sealing and cooling, the tube is mounted on the glass plate (E). The tube is first placed on the plate in such a way that the menisci of the two solutions con-

tained in the enclosed capillaries come within the transverse markings (F). While the tube is held in this position, adhesive tape is applied at the two extreme ends and the tube is fastened to the plate. Two or three tubes may be mounted on the same plate. Both sides of the glass plate may be used.

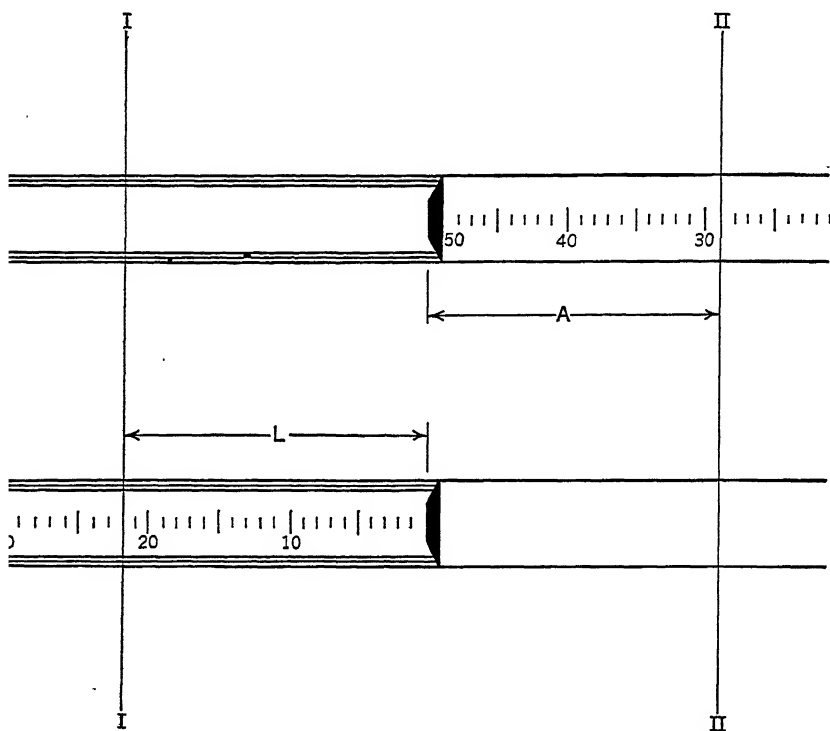


FIG. 57.

Method of Reading. Either the liquid column or the air column may be measured. The liquid column (L) is the distance of the solution between the apex of the meniscus and the nearest reference line situated within the column of liquid (Fig. 57 L). The air column (A) is the distance between the apex of the meniscus and the nearest reference line above the liquid column (Fig. 57 A). The reference lines (F) are distinguished by Roman numerals (I, II, III, IV, V).

Before the readings are taken under the microscope, the position of the meniscus of the standard solution in regard to the nearest reference line is noted (meniscus between reference line I and II [Fig. 57], etc.). After this, the plate with the mounted tubes is placed on the microscope stage with the liquid columns at the left. The meniscus of the standard

solution is brought into focus, and then the nearest reference line is sought. Whether to take readings of the liquid or the air column is decided by whether the reference line within the micrometer scale reading is within the liquid column (*L*) or above the meniscus of the solution (*A*). If the liquid column is chosen, the microscope is focused at the apex of the meniscus (outermost point of the semicircular sharp shadow), and the plate moved until the zero mark of the micrometer scale coincides with this point. Then the microscope is focused upon the chosen reference line and the readings noted (Fig. 57, *LI* : 22).

If the air column is chosen, that is, when a reference line above the meniscus is within the micrometer scale range, again the microscope is focused upon the apex of the meniscus exactly the same as for the liquid column. The plate then is moved so that this point is at the number 50 of the micrometer scale. Without changing the position of the plate the microscope is now focused on the reference line and readings taken (Fig. 57, *AII* : 21).

Readings are repeated not oftener than every twenty-four hours in the beginning and about every two to three days thereafter for about two weeks. Usually, about five readings suffice. An increase in the liquid column is designated as plus (+), a decrease as minus (-). An increase in the air column is regarded as minus (-) and a decrease as plus (+). The results are then tabulated as shown below:

MICROMETER READINGS

| <i>Molarities</i> | <i>Standard Solution</i> | | <i>Unknown</i> | |
|-------------------|--------------------------|------------|----------------|------------|
| | <i>1st</i> | <i>2nd</i> | <i>1st</i> | <i>2nd</i> |
| 0.050 | LII 40 | LII 10 | LIII 10 | LIII 26 |
| 0.075 | AIII 10 | AIII 30 | AIV 24 | AIV 10 |
| 0.100 | LII 30 | LII 20 | AIII 30 | AIII 20 |
| 0.125 | AIV 7 | LIV 7 | LIII 10 | AIII 10 |
| 0.150 | AIII 20 | AIII 4 | LII 20 | AII 10 |

| | | | | <i>Unknown *</i> | |
|-------|-----------------|----------------|-----------------|------------------|--------|
| | <i>Standard</i> | <i>Unknown</i> | <i>Standard</i> | <i>Unknown</i> | |
| | Δ | Δ | | | |
| 0.050 | -30 | +16 | | + | +23 +7 |
| 0.075 | -20 | +14 | | + | +17 +3 |
| 0.100 | -10 | +10 | 0 | 0 | 0 0 |
| 0.125 | +14 | -20 | + | | -17 -3 |
| 0.150 | +16 | -30 | + | | -23 -7 |

* For plotting:

x: molarity of the standard solution;

y: micrometer units;

a: Δ standard solutions;

b: Δ unknown.

INTERPRETATION OF READINGS

From such a table the molarity at which a set of capillaries is *in* or *near* the *isopiestic state* and consequently of *equal* or *nearly equal molarity* can be ascertained in several ways. Such a set of capillaries may exhibit:

(a) *No Change*. The set in which both the standard solution and the solution of the unknown exhibit exactly the same decrease in volume, whereas the other sets in the series show differences.

(b) *Minimum Change*. The set in which there is the least change in volume between the standard solution and the solution of the unknown (*B*); or the set which exhibits the smallest change from the preceding or the succeeding sets in a series (*B'*). In the table above the 0.1 *M* standard solutions fits both cases (*B*, *B'*). In *B* the results may be plotted, particularly when the changes are all in one direction. The molarity of the unknown may thus be approximated.

(c) *Reversal*. When a series of sets is staggered according to increasing molarities as in the table above, the sets containing standard solutions of lower molarity than the unknown will have decreased in volume (—) while those containing standard solution of higher molarity than the solution of the unknown will show an increase (+) in volume of the standard solutions; the set between, at, or near the reversal from minus to plus if standard solutions are compared, or from plus to minus if the solution of the unknown is compared, is regarded as in or near the *isopiestic state* and consequently of *equal* or *nearly equal molarity*. In the table above this is clearly indicated in the 0.1 *M* standard solution.

The condition as given under (a) (no change) occurs very rarely. Thus it seems that the conditions at the surface of two equimolar solutions contained in two separate capillaries will seldom be identical and that difference in concentration of the surface layers may then be responsible for the ensuing volume changes.¹⁴ Usually (b) (minimum change) is observed, particularly when the volumes of all solutions decrease, as happens during the early observations. It is therefore highly advisable to continue the readings, or to repeat the determination with standard solutions of different molarities, until a clear point of reversal as under (c) and as shown in the above table is observable.

Calculation:

$$\text{Molecular weight: } \frac{c}{m}$$

c: grams of sample in 1 liter of solvent;

m: molarity of the standard solution in the set which fulfills at least one of the conditions of isomolarity as given under (a), (b), or (c).

Remarks

The method described herein^{5, 6} is a rigid application of the observations of the botanist L. Errara,¹ who found that the volumes of suspended droplets of salt solution in a closed system invariably increased, while those containing the solvent alone decreased. The method also follows closely the principle involved in the isothermic macromethod of R. A. Robinson and D. A. Sinclair⁹ in which the loss or gain of solvent of two heteromolar solutions contained in separate containers, but placed in the same evacuated desiccator, is followed gravimetrically.

At the suggestion of L. Errara, G. Barger¹ developed his ingenious "microscopical method of determining molecular weight." In this method "a solution of known strength of the substance the molecular weight of which is unknown, is compared with standard solutions of a substance of known molecular weight, a series of drops taken alternately from the two solutions being introduced into a single capillary tube." The chief interference is from the mixing of the droplets either during the filling operation or on standing. The molarities used were from 0.1 to 0.25 *M* solutions, and an accuracy of $\pm 10\%$ is claimed. The method underwent several modifications notably by K. Rast,⁸ who only used 1 drop of each of the two solutions and measured not the actual volume of the drops but the movement of the air bubble separating the two solutions. The molarities employed varied from 0.2 to 1 *M* solutions. A. Friedrich,^{3, 4} in avoiding the rather high concentrations in the foregoing procedure, fixed the 2 drops by eliminating terminal air spaces, while J. R. Spiess¹³ developed an improved method of filling the capillary. Further modifications involve the use of a U-shaped capillary,² actual determination of distillate,¹¹ and adaptation of the method on a macro scale.¹²

For student experiments a system involving a low-boiling solvent (acetone, chloroform, etc.) and allowing observation at atmospheric pressure is preferred. As a standard, azobenzene has been found extremely suitable. Azobenzene solutions of 0.05, 0.75, 0.1, 0.125, and 0.15 *M* are paired with a 0.1 *M* solution of the unknown in the same solvent. The present method possesses several advantages over G. Barger's and its subsequent modifications; e.g., the solutions cannot mix, the sample can be recovered, the changes in volume are much larger and permanent. The apparatus arrangement and technic involved are of utmost simplicity.

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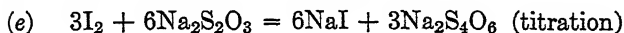
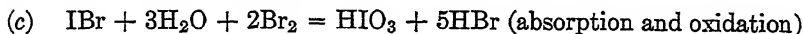
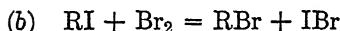
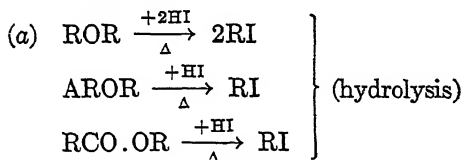
STRUCTURE ANALYSIS

I. DETERMINATION OF ALKOXYL AND ALKIMIDE GROUPS

ALKOXYL GROUPS

Principle

The organic compound containing one or more alkoxy groups (ethers, esters, etc.) is refluxed with hydriodic acid, whereby the alkyl radical attached to oxygen is split off in the form of the corresponding alkyl iodide.³⁷ The resulting alkyl iodide is determined iodometrically.^{9, 20, 33} The method is usually applicable to compounds containing *O*-methyl and *O*-ethyl groups.



Apparatus

Alkoxy Apparatus. The all-Pyrex-glass apparatus illustrated in Fig. 58⁹ consists of four parts: the reaction flask (*A*) with the washer and the side arm (*C*) the delivery tube with a spiral (*E*), and the receiver (*F*).

The reaction flask (*A*) is 2 cm. in diameter; its neck, which carries a standard ground-glass joint, is 6 cm. long and 8 mm. in outer diameter. The carbon dioxide inlet tube (*B*), which extends almost to the bottom of the reaction flask, is 7.5 cm. long and 5 mm. in diameter.

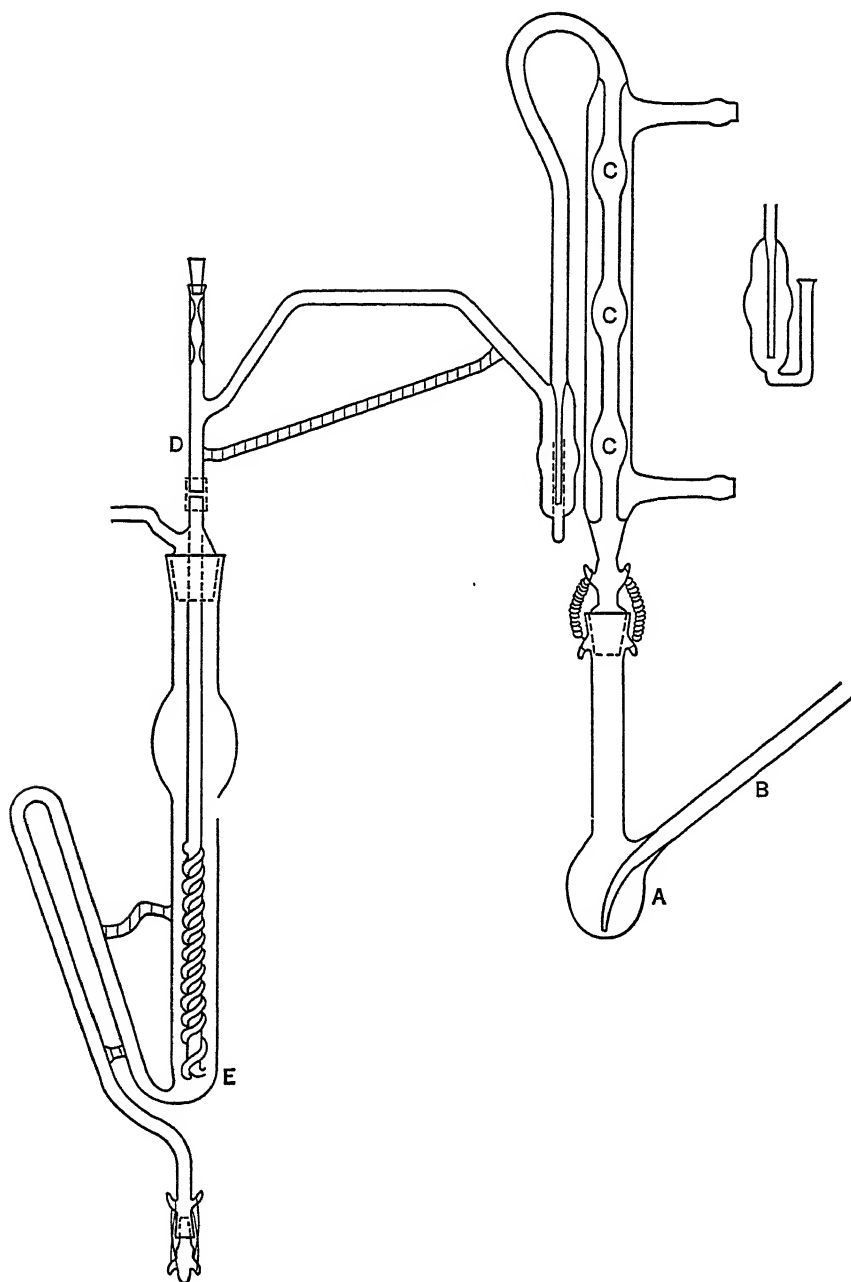


FIG. 58. Alkoxy Apparatus. Inset: Sideview of Washer. Explanation in Text.

The vertical condenser (*C*) is 20 cm. long and 5 mm. in inner diameter; it carries a water jacket and three condensation bulbs. The washer, which is parallel to the condenser, is 5 cm. long and 1.2 cm. in diameter at its widest point. The washer is attached to the condenser by means of a suitably bent tube 5 mm. in diameter. The washer also carries a reinforced side arm of about 10-cm. length which terminates in the upper section of the vertical delivery tube. This section of the delivery tube, which is open at both ends, is 6.5 cm. long and 3 mm. in outer diameter. The detachable lower and longer portion of the delivery tube carries a spiral 9 cm. long and an outlet above its ground-glass joint. It is connected with the delivery tube of the apparatus by means of a piece of rubber tubing, forming a glass-to-glass connection. The upper portion of the receiver widens to 2 cm. and finally terminates in the ground-glass joint of the delivery tube of the apparatus. The bottom of the receiver ends in the siphon tube (*G*), which is 3 mm. in outer diameter. The ascending arm of the siphon is 9 cm. and the descending arm 11.5 cm. long. The descending arm terminates in a vertical section 3.5 cm. long, the outlet of which is provided with a ground-glass stopper placed exactly below the bottom of the receiver.

Kipp Generator. A Kipp generator or a carbon dioxide tank is a suitable source for the carbon dioxide, which is freed from possible halogen vapors by passing it through a gas wash bottle containing a saturated solution of sodium carbonate. A pinchcock is attached to the rubber tubing connecting the Kipp generator with the gas wash bottle to facilitate the regulation of the flow of carbon dioxide.

Glass-Stoppered Pyrex Glass Erlenmeyer Flasks (125-ml. capacity).

Buret. Either a microburet of 10-ml. capacity (p. 51), or still better a well-calibrated 50-ml. macroburet may be used for the 0.01 *N* sodium thiosulfate solution.

Reagents

Hydriodic Acid (sp. gr.: 1.7). Hydriodic acid should be fresh and colorless. All conditions which promote its decomposition and the separation of iodine caused by exposure to light and, more particularly, by access of air, should be avoided. It is preferably kept in an icebox.

Hydriodic Acid (sp. gr.: 1.96).

Phenol. C.P. crystals.

Propionic Acid Anhydride. C.P., boiling point: 64–66° C. at 15 mm. pressure.

Washer Solution. Suspension of red phosphorus in 5% aqueous cadmium sulfate solution.

Sodium Acetate in Glacial Acetic Acid (10%).

Bromine. Free from iodine.

Formic Acid (98 to 100%); melting point: 6 to 8° C.

Aqueous Sodium Acetate Solution (10%).

Sulfuric Acid Solution (10%).

0.01 N Sodium Thiosulfate Solution (p. 56).

Starch Indicator Solution (p. 54).

Procedure

Preparation of the Sample

Solids. Solid substances, previously dried and ground, are weighed in the weighing tube and placed on the bottom of the dry reaction flask. For semi-solids, or substances of syrupy consistency, and non-volatile liquids, a small glass cup, about 4 to 5 mm. in diameter and height, which fits conveniently into the neck of the reaction flask, is used. A piece of glass in the shape of a semicylindrical boat or trough with open ends, made from glass tubing of suitable diameter by cutting it lengthwise, or a piece of platinum foil molded to a boat-like shape, also serves the purpose.

Liquids. Volatile liquids are weighed in a small glass cup with a ground-glass stopper, or in a weighing pipet (p. 46). The weighed capillary pipet is centrifuged, cut just above the meniscus of the liquid, and both halves are then placed in the reaction flask.

Introduction of the Sample and Solubility Tests. A few crystals of phenol and 6 to 10 drops of propionic acid anhydride are added to the substance in the reaction flask, which is shaken to effect solution of the sample in the solvent. If the substance does not completely dissolve, the reaction flask is cautiously heated over a steam bath or over a very small flame to about 60 to 80° C. If complete solution still does not take place, a little more of the solvents is added until the substance has completely dissolved. Since this additional solvent will considerably lower the concentration of the hydriodic acid, a corresponding amount of hydriodic acid of sp. gr. 1.96 must be added to restore its original concentration. After allowing the solution to cool, a few Alundum beads of size 16 are placed in the reaction flask and then about 2 ml. of hydriodic acid (sp. gr.: 1.7) is added dropwise from a pipet while the flask is rotated to wash down any particles of substance that may adhere to the wall.

Preparation of the Apparatus and Heating. The washer of the apparatus is filled with 0.5 ml. of washer solution and stoppered with a cork. Then 4 to 5 ml. of glacial acetic acid-sodium acetate solution, to which 6 to 8 drops of bromine has been added, is placed into the receiver. The

glass spiral is inserted into the solution, the reaction flask is connected as quickly as possible to the condenser, through which water is circulated, and the side arm is attached to the source of carbon dioxide, the flow of which is reduced to a slow stream. The flow of carbon dioxide is best adjusted by inserting a stopcock having a fine groove between the side arm and the carbon dioxide generator. The reaction flask is allowed to stand at room temperature for thirty minutes,¹ after which a small flame is placed under the flask and so regulated that the temperature of the solution remains below the boiling point for another thirty minutes. Then the flame is slowly raised and the solution is brought to boiling and maintained at that temperature for one hour or sometimes even longer (two to three hours). About fifteen minutes prior to the completion of the determination, the rate of carbon dioxide passing through the system is increased; the water in the condenser is allowed to drain off, and after about fifteen minutes the flame is removed.

Titration. The titration procedure³³ is the same as in the iodometric determination of iodine (p. 174). After completion of the heating and sweeping-out process the receiver is emptied by washing its contents into a ground-glass-stoppered Erlenmeyer flask which contains 5 ml. of aqueous sodium acetate solution. The excess of free bromine is destroyed by adding a few drops of formic acid while shaking the Erlenmeyer flask. The flask is allowed to stand for a few minutes, after which it is stoppered and shaken well to remove the last traces of bromine from the solution. If, after this treatment, the solution is not completely decolorized, another drop of formic acid is added and the flask is shaken again. Then 2 ml. of 10% potassium iodide solution is added and the solution is acidified with 3 ml. of 10% sulfuric acid; the flask is again stoppered and shaken. In the event of a high methoxyl value, which usually is evidenced by the intensity of the color of the liberated iodine, the time of standing is extended from the usual five minutes to fifteen minutes, before the solution is titrated with 0.01 *N* sodium thiosulfate solution.

Time:

| | <i>Minutes</i> |
|--|----------------|
| Weighing of the sample..... | 10 |
| Preparation of the apparatus and introduction of the sample..... | 30 |
| Heating..... | 120 |
| Titration..... | 15 |
| Total..... | 175 |

Calculation:

Log of ml. of 0.01 *N* sodium thiosulfate solution,
 Plus log of factor,
 Plus negative log of weight of sample;
 Antilog of total = percentage of alkoxyl.

Factors:

Methoxyl: 0.05172; log, 71366.
 Ethoxyl: 0.07510; log, 87564.

ALKIMIDE GROUPS**Principle**

The organic compound containing one or more *N*-alkyl groups (primary, secondary, and tertiary amines, etc.) is first refluxed with hydriodic acid to form the respective quaternary alkyl ammonium iodide, which then is subjected to pyrolysis. The lower alkyl radicals (methyl, ethyl, etc.) are thus split off from the nitrogen in form of their alkyl iodides,^{10, 14} which are then determined iodometrically.

- $$(a) \quad >N-R + HI \rightarrow >N-R \cdot HI \xrightarrow{\Delta} RI \text{ (pyrolysis)}$$
- $$(b) \quad RI + Br_2 = RBr + IBr$$
- $$(c) \quad IBr + 3H_2O + 2Br_2 = HIO_3 + 5HBr \text{ (absorption and oxidation)}$$
- $$(d) \quad HIO_3 + 5HI = 3I_2 + 3H_2O$$
- $$(e) \quad 3I_2 + 6Na_2S_2O_3 = 6NaI + 3Na_2S_4O_6 \text{ (titration)}$$

Apparatus

The determination^{10a-d} is carried out in an apparatus made of Pyrex glass (Fig. 59). It consists of an olive-shaped reaction flask (*a*) of about 5-ml. capacity, which has a side inlet (*b*) 12 cm. long and 6 mm. in diameter for the introduction of the sample and the carbon dioxide. The delivery tube (*c*) is 12 to 13 cm. long and about 6 mm. in diameter. It is fused to the reaction flask in a position to form an angle of about 45 degrees with the side inlet. The delivery tube continues in an almost horizontal line for about 8 cm. and then it is bent downward to extend vertically for 11 cm., when it is again bent horizontally for a length of 7 cm.; 2.5 cm. above this bend the vertical portion (*d*) of the right side arm (*e*) of the three-way stopcock is fused on. The delivery tube is then bent upward and at the same time widened to form the condensation bulb (*f*), which is 1.5 cm. in diameter and 3 cm.

long. The extension of the delivery tube connects this condensation bulb with the horizontal left side arm (*e'*) of the three-way stopcock. Thus the two side arms of the stopcock and the delivery tube form a rectangle, the lower portion of which is heated during the determination by immersion in hot water. Beyond the connection of the delivery tube with the left arm of the stopcock the delivery tube continues horizontally for about 5 cm., after which it is again bent downward at right angles and extends into the washer (*g*) as a capillary of about 1-mm. inner diameter. The side arm of the washer is connected to the vertical

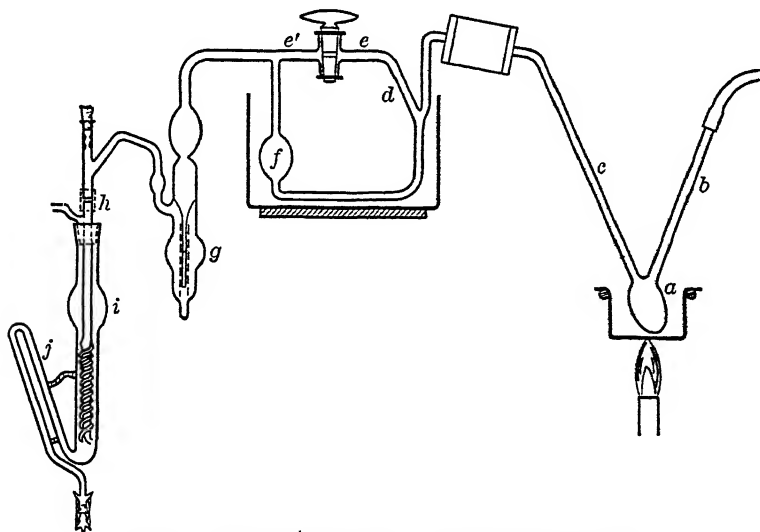


FIG. 59. Alkimide Apparatus. Explanation in Text.

delivery tube (*h*), which is 6.5 cm. in length, 3 mm. in diameter, and open at both ends.

The detachable lower and longer portion of the delivery tube (*i*) carrying a spiral, and the siphon-receiver (*j*), as well as all other apparatus, such as the Kipp generator, Erlenmeyer flasks, and titration equipment, are the same as in the alkoxyl determination (p. 241).

Reagents

Aside from the reagents listed in the alkoxyl determination the following two reagents are necessary:

Aqueous Gold Chloride Solution (5%).

Ammonium Iodide. C.P.

Procedure

Preparation of the Sample and Apparatus. The preparation of the sample, including the solubility tests, and the cleaning and drying of the alkimide apparatus are the same as in the alkoxy determination. After the washer has been filled with 0.5 ml. of 5% sodium thiosulfate solution, the substance is introduced into the reaction flask and is dissolved in the phenol-propionic anhydride mixture; a spatula point of ammonium iodide is added, and then 1 or 2 drops of gold chloride solution and 2 ml. of hydriodic acid. The receiver is filled with 4 to 5 ml. of glacial acetic acid-sodium acetate solution, to which 6 to 8 drops of bromine has been added. After insertion of the spiral of the delivery tube into the receiver, and with the pinchcock between the inlet tube and the source of carbon dioxide closed, the rubber tubing is drawn over the side inlet tube, into which a small sealed tube has been inserted. The stopcock is opened and the current of carbon dioxide is regulated so that no more than 2 bubbles at a time rise in the receiver.

Heating. The reaction flask is placed in a metal pan containing powdered copper oxide and a thermometer. The lower portion of the rectangle is immersed in a dish of water which is heated to 90° C. The pan is heated very slowly to a temperature of 360° C.; this gradual heating should require about one hour. The heating at 360° C. is continued until all the hydriodic acid has been distilled off, whereupon the flame is extinguished and the apparatus is allowed to cool to room temperature. The stopcock is then turned crosswise, so that the vertical bore faces the washer (*g*). Next, the flow of the carbon dioxide is shut off, the rubber tubing is removed from the inlet tube, and the hydriodic acid in the lower part of the rectangle is siphoned back into the reaction flask by applying suction by mouth at this tube. About 0.5 ml. of fresh hydriodic acid is introduced through the vertical bore of the stopcock and is also siphoned back. The receiver is then exchanged for another one which has been freshly filled, and the stopcock is again turned to its original position. Carbon dioxide is passed through the apparatus and the heating is repeated at least once more as described above.

Titration. The titrations are carried out in exactly the same manner as described in the alkoxy determination (p. 243).

Calculation:

Log of ml. of 0.01 *N* sodium thiosulfate solution,
 Plus log of factor,
 Plus negative log of weight of sample;
 Antilog of total = percentage of alkimide.

Factors:

Methyl, 0.02503; log, 39863.
 Ethyl, 0.04839; log, 68476.

Remarks

O-Alkyl

Iodometric Methods. The iodometric determination of *O*-alkyl groups as presented in this manual is the method of A. Elek,⁹ which incorporates several improvements over the gravimetric method as devised by F. Pregl^{28, 30} and the iodometric method of F. Vieböck and co-workers.³³ Both the gravimetric and the iodometric methods have been the subject of thorough investigation.^{1, 2, 4, 6, 8, 11, 13, 14, 20, 23, 24, 31, 35}

The original Zeisel methoxyl macromethod,³⁷ as adapted and modified for microdeterminations by F. Pregl,^{28, 30} consisted in heating the substance with hydriodic acid, driving off the alkyl iodide with carbon dioxide, absorbing it in alcoholic silver nitrate solution, and determining the silver iodide gravimetrically. Later F. Vieböck and co-workers³³ shortened the last part of the procedure by iodometric determination of the alkyl iodide distilling over.

The modified apparatus of D. R. Rigakos²⁹ consists in the introduction of a ground-glass joint between the reaction flask and the outlet tube, and of a capillary leading from the side arm near the bottom of the reaction flask. The same modification of the apparatus was described several years later by F. Neumann²⁵ for highly methylated carbohydrates. E. P. Clark⁶ has described an apparatus having ground-glass joints and a capillary side arm, which can be used for macro as well as microdeterminations. J. J. Chinoy⁵ has also constructed a modified apparatus with a ground-glass joint fitting into the reaction flask and with an extension ending in a glass ladle, or cup, which facilitates the introduction of the sample. These improvements have been applied to solid and syrupy substances and to liquids whose boiling points are above that of hydriodic acid.

A. F. Colson⁷ has devised an apparatus for liquids having boiling points lower than that of the hydriodic acid. This apparatus consists of a vertical tube connected above the reaction flask; the tube is filled with small glass beads moistened with hydriodic acid. Two washing tubes are connected with the train to entrap any hydriodic acid that might have distilled over; hydriodic acid of sp. gr. 1.96 is used.

M. Lieff and co-workers²² have described a modified apparatus which is stated to be more practical for the iodometric method. The Pregl type of receiver is replaced by an absorption tube, containing four *pockets*, which is attached to the outlet tube of the Pregl type of apparatus by a ground-glass joint in an inclined position. A novel type of receiver has been described by B. E. Christensen and co-workers.⁸

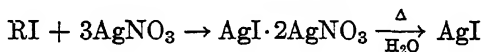
In the determination of alkoxy groups it is important that there be thorough absorption, and in the titrimetric method complete oxidation

of the alkyl iodide to iodate. This is achieved by means of a long and slow passage of the alkyl iodide through the absorption liquid. For this purpose a glass spiral, consisting of about twelve turns, was devised by A. Elek.⁹ It is attached to the outlet tube, which is immersed in the absorbent contained in a modified L. Kahovec¹⁵ type of receiver.

A. Friedrich¹⁰ states that the method is quite accurate if the hydriodic acid is pure, and that the substance should be brought into solution before the addition of the hydriodic acid. G. M. Ware³⁴ reports that, if the substance contains more than two methoxyl groups, the hydriodic acid of sp. gr. 1.7 should be replaced by hydriodic acid of sp. gr. 1.96 in order to obtain reliable results. For highly methylated carbohydrates F. Arndt¹ and F. Neumann²⁵ mention that methoxyl values which are 1 to 2% low have often been reported; they attribute this discrepancy to the fact that the reaction flask is heated over a free flame and that as a consequence the substance in the flask is more or less *caked*. According to them, this caked portion of the substance does not react with the hydriodic acid, and the variation in the degree of caking is responsible for the non-reproducibility of values obtained from the same sample, especially for polymeric carbohydrates. Therefore, an oil bath with gradual elevation of the temperature is used to circumvent this detrimental effect.

V. Bruckner⁴ obtained correct results in some cases without the use of any solvent. F. Pregl^{28, 30} and others¹⁸ mention separate solubility tests before the addition of hydriodic acid, but these are obviously not feasible when only a small amount of substance is available.

Gravimetric Methods.^{10, 28, 30, 34, 36} The iodometric method of A. Elek,⁹ as described in this manual, may also be used for the gravimetric determination of alkoxy groups in organic compounds, particularly for the occasional checking of the iodometric method. In this method the siphon of the receiver (Fig. 58*F*) is omitted, and a 4% alcoholic silver nitrate solution is used as the absorbing agent.



The procedure remains the same. After completion of the heating and sweeping-out, the apparatus is raised sufficiently so that the tip of the delivery tube is about 2 cm. above the solution in the receiver. Next, the cork is removed from the top and the delivery tube is rinsed from above, inside and outside, with dilute nitric acid and alcohol. Should particles of silver iodide still adhere to the delivery tube, it is again rinsed alternately with these reagents. Mechanical removal with the aid of a feather or rubber policeman should be resorted to only

after attempts to remove the last particles by rinsing have failed. Five drops of concentrated nitric acid is added to the solution in the receiver and the receiver is heated on the steam bath until the contents begin to boil. Then the receiver is cooled under the tap and when cool the silver iodide precipitate is filtered with a halogen filter tube; the precipitate is washed, dried, and weighed as described in the halogen determination on p. 157.

An empirical correction of 0.06 mg. silver iodide for each milliliter of alcoholic silver nitrate solution must be added to correct for incomplete precipitation of the alkyl iodide.¹⁰

Calculation:

Log of weight of precipitate,
Plus log of factor,
Plus negative log of weight of sample;
Antilog of total = percentage of methoxyl or ethoxyl.

Factors:

Methoxyl, 0.1321; log, 12096.
Ethoxyl, 0.1918; log, 28287.

S-Alkyl. The possibility of applying the conventional semi-micro⁶ and micro alkoxyl³³ methods for the determination of *S*-alkyl groups (thio ethers) has been investigated repeatedly. Satisfactory^{9, 28, 30} as well as unsatisfactory^{1, 3} results have been reported. Usually a longer heating period (three to eight hours) is necessary.

N-Alkyl.^{10, 11, 28, 30} The alkylimide method described in this manual is a modification of the method devised by A. Friedrich.¹⁰ Great caution has to be exercised in interpreting the results. Some substances yield only one-half or one-third of their number of *N*-alkyl radicals, such as certain alkaloids and complex *N*-heterocyclic compounds.

Hydriodic Acid.^{8, 10, 28, 30, 32} Most important in any of the foregoing O-, S-, or N-alkyl determinations is the quality of the hydriodic acid (sp. gr.: 1.7) employed. Several suggestions for its preparation and purification have been made.^{6, 10} According to A. Friedrich¹⁰ the purification and regeneration of this acid are best accomplished by refluxing commercial hydriodic acid with red phosphorus until complete decolorization has taken place. The acid is then distilled in an all-glass apparatus in an atmosphere of nitrogen. E. P. Clark⁶ suggests the following method for the preparation of the acid: 254 grams of iodine and 185 grams of water are heated to about 50° C. in a 500-ml. flask having a ground-glass condenser, and 66 grams of 50% hypophosphorous acid (H_3PO_2), which must be free from sulfate, is added

in portions at such a rate that the mixture is boiling continuously until the iodine is reduced. Heat is then applied to the flask and the boiling is continued for three hours, during which time a current of carbon dioxide is passed through the solution. The position of the condenser is changed to allow distillation, and the constant-boiling hydriodic acid is collected. The yield is 447 grams. The hydriodic acid thus prepared is stored in dark bottles and preserved by the addition of a little 50% solution of hypophosphorous acid (about 1 ml. per 450 grams).

Under some conditions, for instance, in the determination of alcohols or of glycerol in aqueous solutions, or when too large an amount of solvent had to be used, it is necessary to employ hydriodic acid of sp. gr. 1.96 in order to maintain and retain a specific gravity of 1.7 in the reaction mixture.

OTHER METHODS

Methoxyl and *ethoxyl* groups may also be determined *simultaneously*. The alkyl iodides as formed by the hydrolysis with hydriodic acid in the usual manner are collected in an alcoholic solution of *trimethylamine*; thus tetramethyl ammonium iodide and trimethylethyl ammonium iodide are formed.¹⁹ Since the former is almost insoluble in absolute alcohol and the latter is readily soluble, the separation of the salts is possible.³⁶ After the addition of dilute nitric acid and silver nitrate to the separated salts, the iodine is precipitated and determined gravimetrically as silver iodide.

Pyridine may also be used for the absorption of alkyl iodides,^{17, 21, 23} both for qualitative²³ and for quantitative determinations. Application of the original micro alkoxyl determination method as devised by F. Pregl^{28, 30} to the *quantitative determination* of minute amounts of *ethyl alcohol* in aqueous solutions (steam distillates of human brains) has been reported by A. O. Gettler, J. B. Niederl, and A. A. Benedetti-Pichler.^{12, 26}

The alkyl iodides, as obtained in *O*-, *S*-, and *N*-alkyl determinations, may be identified as 3,5-dinitrobenzoates, or as α -naphthylamine derivatives.¹¹

Applying appropriate modifications to the conventional micro Zeisel apparatus, J. B. Niederl and M. Brenner²⁷ succeeded in the conclusive identification of *ethylene* as given off by ripening fruits, thus indicating that such an apparatus is a valuable research instrument in certain isolation and identification procedures.^{12, 26, 27}

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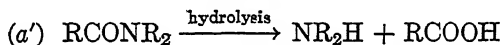
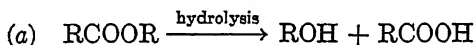
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II. DETERMINATION OF ACYL GROUPS

ALKALIMETRIC METHOD

Principle

The organic substance containing *O*-acyl or *N*-acyl groups (esters, amides, etc.) is hydrolyzed in either an acidic or alkaline medium, depending upon the solubility of the substance. After hydrolysis the volatile acidic hydrolysis products are subjected to steam distillation and the distillate is collected in several portions. The distillates are then titrated separately with 0.01 *N* sodium hydroxide solution, and from the total amount of standard alkali consumed the percentage acyl is calculated.^{10, 17, 19}



Apparatus

Bubble Counter and U-Tube. These are the same as used in the carbon and hydrogen determination (p. 104). The bubble counter is filled with 50% potassium hydroxide solution and the U-tube with Ascarite.

Hydrolysis Apparatus (Fig. 60). This is an all-Pyrex glass or quartz apparatus consisting of the three-necked reaction flask, the gas inlet tube, the funnel, and the condenser. The *reaction flask* has a capacity of 60 ml. and consists of the reaction chamber, which is 5 cm. in diameter and 4.5 cm. in height, and has three necks. The neck at the left, 9.5 cm. long and 7 mm. in outer diameter, serves for the insertion of the gas inlet tube, the descending portion of which is 18 cm. and the horizontal portion 6 cm. long. This *inlet tube* carries on the outside a ground-glass joint which fits into the neck at the left. The center neck is also 9.5 cm. long, but is 1.2 cm. in outer diameter; it is provided with an outer ground-glass joint into which fits the inner ground-glass

joint of the funnel. The *funnel* has an overall length of 16 cm.; the upper portion has a capacity of 8 ml. and is 8.5 cm. long and 1.5 cm. wide; the stem is 8 cm. long and 4 mm. in diameter. The funnel carries two ground-glass joints, of which the upper fits into the neck of the reaction flask, the lower one inside serving as a seal for the *plunger*; the plunger is 12 cm. long and 4 mm. in diameter and is provided with an inner ground-glass joint. The *condenser tube* is 50 cm. long and 8 mm. in outer diameter and carries a water jacket 30 cm. long and 2.2 cm. in outer diameter. The condenser tube terminates on one end in an outlet 7 cm. long and 8 mm. in diameter and bent at 135 degrees. This outlet tube is provided with a ground-glass joint which fits into

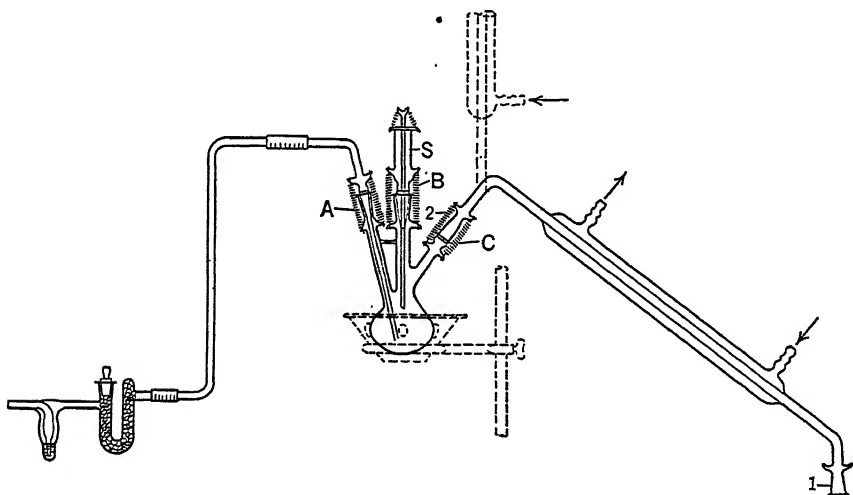


FIG. 60. Acyl Apparatus. Explanation in Text.

the neck at the right of the reaction flask. The opposite end of the condenser tube terminates in a similar outlet tube, which is bent in the same direction, but only at 90 degrees. Thus the condenser can serve either as a vertical reflux condenser or as an inclined water condenser. All ground-glass joints carry glass hooks for the attachment of steel springs.

Water Bath. Either a metal bath or a 1-liter beaker can be employed.

Pipets. Of 0.5, 1.5 and 10-ml. capacity; or a 10-ml. pipet graduated in 0.1 ml.

Titration Equipment. The same as described under "Standard Solutions" (p. 51).

Reagents

Aqueous Sodium Hydroxide Solutions: 1 *N* and 5 *N*.

Alcoholic Sodium Hydroxide Solution. Four grams of sodium hydroxide pellets is dissolved in 50 ml. of distilled water; the resulting solution is mixed with 50 ml. of methyl alcohol previously refluxed and redistilled over solid potassium hydroxide.

Concentrated Sulfuric Acid (sp. gr.: 1.84).

Dilute Sulfuric Acid. To 200 ml. of distilled water is added 100 ml. of concentrated sulfuric acid.

Sulfonic Acid Solution. Twenty-five grams of *p*-toluene sulfonic acid is dissolved in 100 ml. of distilled water.

Metaphosphoric Acid. This acid is used as a lubricant for the ground-glass joints. It is prepared by the addition of small amounts of water to phosphorus pentoxide.

Pyridine. C.P.

Barium Chloride. Crystals, reagent quality.

0.01 *N* Sodium Hydroxide Solution (p. 56).

0.01 *N* Acid Solution. Either potassium biiodate or hydrochloric acid solution may be used (p. 54).

Phenolphthalein Indicator Solution (1%; p. 54).

Procedure

Solubility Tests. In order to select the proper hydrolyzing agent, the substance is first tested for its solubility in the four principal hydrolyzing agents, i.e., aqueous sodium hydroxide solution, alcoholic sodium hydroxide solution, or dilute sulfuric and sulfonic acid solutions. The hydrolyzing agent in which the substance is most readily soluble is then chosen for the hydrolysis of the substance in question. Should the substance be insoluble in all four reagents, pyridine may be used as additional solvent.

Preparation of the Sample. *Solids* are weighed and introduced through the center neck into the reaction flask of the hydrolysis apparatus by means of the weighing tube. *Volatile liquids* are weighed in the usual weighing pipets, while less volatile liquids, semi-solids, and syrups are weighed in capillaries open at both ends, one end of which may be drawn out to a fine capillary. The filled and weighed capillary is cut above the meniscus of the liquid, and both bulb and stem are thrown into the reaction chamber of the hydrolysis apparatus which, with the condenser and inlet tube already attached, has been made ready for the determination.

Preparation of the Apparatus. The apparatus must be clean and dry before use. The bubble counter is connected to an oxygen or nitrogen tank and the speed of the bubbles is adjusted to 1 bubble per second. The reaction flask is connected to the condenser, which is now in a vertical position, and then the gas inlet tube is inserted into the neck at the left of the reaction flask. The ground-glass joints are previously lubricated with metaphosphoric acid. Next, the hydrolyzing agent is added to the substance in the reaction flask through the center neck. (If the substance is volatile the hydrolyzing agent is introduced first and the capillary with the substance afterwards.) The following amounts of hydrolyzing agent are used:

Acid Hydrolysis: 1 ml. *Alkaline Hydrolysis:* 1 ml. aqueous or 4 ml. of the alcoholic sodium hydroxide solution. After the addition of the hydrolyzing agent, the funnel, without the plunger and with its ground-glass joint on the outside properly lubricated, is inserted into the center neck and the gas inlet tube is connected to the bubble counter. Then the plunger is inserted into the upper portion of the funnel and a seal is formed by the introduction of 1 ml. of water into the upper portion of the funnel.

Hydrolysis. The reaction flask is completely immersed in the water bath and the water is brought to boiling; the heating is continued for twenty minutes, after which the water bath is removed and the apparatus is allowed to cool. The inside of the condenser is rinsed with 5 ml. of distilled water, which is allowed to drain into the reaction flask and then the condenser is removed, washed with 100 ml. of distilled water, and reconnected to the neck at the right with the wide-angle outlet tube, so that the condenser is inclined downward, as shown in Fig. 60. The direction of the water circulating through the cooling jacket is also changed accordingly. (If the hydrolysis was performed with alcoholic sodium hydroxide solution, the alcohol—4 ml. of distillate—is now distilled off. After the removal of the alcohol the condenser is again rinsed and washed with distilled water as described above.)

Distillation. After re-attachment of the condenser so that it again faces downward, the following reagent is introduced into the upper portion of the funnel:

- (a) Sulfuric acid hydrolysis: 1 ml. of 5 *N* sodium hydroxide solution.
- (b) Sulfonic acid hydrolysis: 0.5 ml. 1 *N* sodium hydroxide solution.
- (c) Alkaline hydrolysis (either aqueous or alcoholic): 1 ml. dilute sulfuric acid.

The plunger is then lifted sufficiently to allow the reagent to flow into the reaction flask; this is followed by rinsing of the funnel with 2 ml. of distilled water, after which several pieces of Alundum are added to the reaction mixture; the plunger is re-inserted and 7 ml. of distilled water is introduced into the upper portion of the funnel. Using a small gas flame, distillation is started at a rate so that about 1 ml. per minute distills into the receiver, which may be a steamed-out and marked 125-ml. Erlenmeyer flask of Pyrex glass, or a similarly treated Pyrex glass graduate cylinder with a funnel. When the volume of the reaction flask has decreased to about 2 to 3 ml., more distilled water is slowly added, without interrupting the distillation, by lifting the plunger and allowing the distilled water in the funnel to run into the reaction flask. The funnel is again filled with 7 ml. of water and the above procedure is repeated until the total amount of the distillate collected in the receiver has reached a volume of about 20 ml. The receiver is then exchanged for another one, and this time a total of 15 ml. distillate is collected. This is repeated twice, about 5 ml. being collected each time, to give a total of four fractions of distillate: first, 20 ml.; second, 15 ml.; third and fourth, 5 ml. each. The time required for the distillation of the four fractions is about forty minutes.

Titration. The four distillates should be titrated separately. The first and the second may be titrated while distillation is still in progress. A few milligrams of barium chloride are added to the distillate, which is then quickly heated to boiling; no turbidity must occur. A few drops of indicator solution are added and the hot solution is titrated with 0.01 *N* sodium hydroxide solution to a faint pink coloration (see p. 67). The remaining distillates are titrated in exactly the same manner.

Calculation:

Log of total ml. of 0.01 *N* sodium hydroxide solution (sum of all four titrations),

Plus log of factor,

Plus negative log of weight of sample; $M \rightarrow \frac{100}{M}$

Antilog of total = percentage acyl. $\frac{100}{M} \times \frac{1}{100} \times 100 = \frac{100}{M}$

Factors:

Acetyl ($\text{CH}_3\text{CO}-$): 0.4302; log, 63367.

Benzoyl ($\text{C}_6\text{H}_5\text{CO}-$): 1.0504; log, 02135.

IODOMETRIC METHOD

Principle

The organic substance containing *O*- or *N*-acetyl groups is hydrolyzed by means of *p*-toluenesulfonic acid in a closed system. The acetic acid formed after steam distillation is determination iodometrically.⁴

- (a) $\text{CH}_3\text{COOR} \xrightarrow{\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}} \text{ROH} + \text{CH}_3\text{COOH}$ (hydrolysis)
 (b) $\text{CH}_3\text{CONR}_2 \xrightarrow{\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}} \text{NR}_2\text{H} \cdot \text{C}_7\text{H}_7\text{SO}_3\text{H} + \text{CH}_3\text{COOH}$
 (c) $6\text{CH}_3\text{COOH} + 5\text{KI} + \text{KIO}_3 = 3\text{I}_2 + 3\text{H}_2\text{O} + 6\text{CH}_3\text{COOK}$ (titration)

Apparatus

Acetyl Apparatus (Fig. 61). This consists of a distilling flask (a) to which a suitably constructed all-glass dropping funnel (b) is connected by a ground-glass joint. The ascending side arm (c) of the distillation flask is provided with a still head, and its downward section is connected to the inner tube of a water condenser, through which cold water is circulated during the distillation. Attached to this condenser is the receiver (d), which is provided with a suitable side arm for attachment to the vacuum pump. The apparatus is constructed wholly of Pyrex glass, the joints being especially ground to make them vacuum tight with only water as lubricant. The connection between the side arm of the flask and the condenser is made glass-to-glass and sheathed in steamed rubber tubing in order to provide sufficient flexibility to permit tapping of the flask. It is important that these parts be made of glass tubing having the same outside diameter as the side arm of the flask to facilitate air-tight connections.

Titration Equipment. See "Standard Solutions" (p. 51).

Reagents

Sulfonic Acid Solution (25%); (p. 255).

Potassium Iodide. C.P. crystals.

Potassium Iodate Solution (4%). Four grams of potassium iodate, of reagent purity, is dissolved in 100 ml. freshly boiled distilled water.

0.01 N Iodine Solution. This is prepared by diluting a 0.1 *N* iodine solution, or by dissolving 1.27 g. of analytical reagent iodine in a solution of an equal weight of analytical reagent potassium iodide in freshly boiled distilled water and diluting to 1 liter.

0.01 N Sodium Thiosulfate Solution (p. 56).

Starch Indicator Solution (1%) (p. 54).

Procedure

Preparation of the Apparatus. The entire apparatus, with the exception of the rubber connections, which are well steamed, is thoroughly

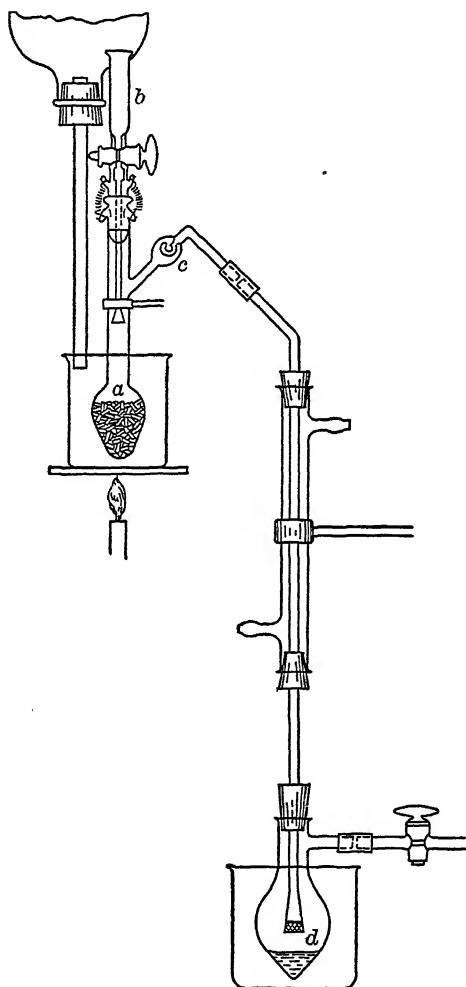


FIG. 61. Acetyl Apparatus. Explanation in Text.

cleaned with cleaning solution, well rinsed, and dried. Between successive determinations thorough rinsing with distilled water is sufficient and only the distilling flask need be dried.

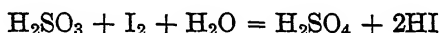
Charging of the Distilling Flask. The sample is weighed in the weighing tube and transferred to the bottom of the distilling flask, which is then filled about three-fourths full with short pieces (4 mm.) of Pyrex glass rods. The ground-glass joint of the funnel is moistened with distilled water, inserted in the distilling flask, and fastened with short wire springs. Two milliliters of sulfonic acid solution is added through the funnel, and the stopcock is sealed with several drops of distilled water which is introduced through the funnel. When analyzing compounds containing halogen, 2 to 3 mg. of silver sulfate is added. The side arm of the flask is attached to the condenser with the freshly rinsed short rubber tubing, thereby effecting a glass-to-glass connection. The receiver is charged with 5 ml. of 0.01 *N* iodine solution to which about 1 gram of powdered potassium iodide had been added, and then it is attached to the rubber stopper on the lower end of the condenser; the height of the flask is adjusted so that the sintered-glass plate is approximately 1 cm. above the surface of the liquid. The side arm of the receiver is capped with a well-washed rubber nipple. The receiver is cooled by immersing it up to the side arm in a beaker of finely cracked ice, which is renewed from time to time during the hydrolysis. Finally, the distilling flask is tapped repeatedly to mix the sample intimately with the acid.

Heating. An asbestos board is placed as a shield between the burner and the condenser. The mixture is heated by bringing the water in the surrounding beaker to boiling. The level of water in the beaker is maintained during the period of heating by using an inverted bottle containing water, held well above the apparatus, and having a 1-cm. tube reaching just to the desired level in the beaker. During the course of the heating the flask is tapped vigorously at intervals in order to agitate its contents. Hydrolysis is continued for one hour for *O*-acetyl and approximately three hours for *N*-acetyl compounds. At the end of the hydrolysis the hot water is siphoned out of the beaker and replaced by ice-cold water. After cooling the apparatus for about five minutes, an aspirator is connected through a manometer and stopcock to the side arm of the receiver and the system evacuated to a pressure of 50 to 60 mm. The receiver is lifted, together with its cooling beaker, until the sintered plate is about 2 mm. from the bottom of the receiver and the water surrounding the distilling flask is heated. At first a few small bubbles will pass through the iodine solution, but the bubbling stops as soon as the pressure is equalized throughout the system. When the liquid in the distilling flask has completely distilled over, aided by occasional tapping, 1.5 to 2 ml. of water is run in through the funnel without breaking the vacuum or interrupting the heating. After the distilling flask has

become dry, a second and finally a third portion of water are introduced in a similar manner. Heating is then continued until the distilling flask is completely dry and for about ten minutes thereafter. The receiver is then lowered with a gentle rotatory motion, until the sintered plate is 2 cm. above the solution. Next, the stopcock between the receiver and the manometer is closed and the connection between the stopcock and manometer is broken; by slowly opening the stopcock, the system is brought back to atmospheric pressure, after which the burner is extinguished.

Transfer of the Distillate and Titrations. The condenser is disconnected from the flask and rinsed three times with a small amount of distilled water. Drainage through the sintered-glass plate may be accelerated by application of slight suction through the side arm of the receiver. The outside of the lower part of the condenser is also washed with a small amount of distilled water, but the total volume of solution in the receiver should not exceed 20 ml. Then the iodine solution in the receiver is titrated with 0.01 *N* sodium thiosulfate solution in the usual manner (*first titration*). After completion of this titration, 2 ml. of the potassium iodate solution is added to the solution in the receiver, which is immediately stoppered with an Ascarite tube and placed in a beaker of water at about 35° C., in which it is allowed to stand for twenty minutes. Then the solution is titrated once more with the 0.01 *N* sodium thiosulfate solution as before (*second titration*).

Correction for Sulfur Dioxide. A small amount of sulfur dioxide might occasionally be formed as an interfering by-product in the hydrolysis. To correct for this, the receiver is originally charged with 5 ml. of 0.01 *N* iodine solution. This solution causes the conversion of the sulfur dioxide, or sulfurous acid, into sulfuric acid and hydriodic acid as follows:



As a control, 5 ml. of the same 0.01 *N* iodine solution, to which 1 gram of potassium iodide and a few drops of acetic acid have been added, is titrated separately with the 0.01 *N* sodium thiosulfate solution (*third titration*). When measuring the 0.01 *N* iodine solution it is necessary to wait a few minutes before reading the meniscus. Usually, there ought to be no difference between the first and the third titration; differences up to 0.05 ml. are permissible, but if the difference is larger, the analysis is rejected. The difference, multiplied by 2, to account for the dibasicity of the sulfuric acid, is deducted from the second or main titration.

Calculation:

Log of net ml. 0.01 *N* sodium thiosulfate solution (second titration),
Plus log of factor (63370),
Plus negative log of weight of substance;
Antilog of total = percentage acetyl.

Remarks

The alkalimetric *O*- and *N*-acyl determination presented in this book is the method of H. Kuhn and H. Roth,¹⁰ while the iodometric *O*- and *N*-acetyl determination given here is the method of A. Elek and R. A. Harte.⁴

Since the appearance of the micromethod of F. Pregl and A. Soltys,¹⁶⁻¹⁸ who used *p*-toluene sulfonic acid as hydrolyzing agent, there have been two significant attempts to modify this determination in order to overcome certain inherent defects. The first of these is the method of A. Friedrich and co-workers,^{7, 8} who simplified the apparatus and the manipulation. The use of a Claisen flask as hydrolyzing vessel and the omission of the U-tube make the apparatus simpler, and the replacement of the alkalimetric titration by the more efficient iodometric method is a desirable improvement. The regulation of the current of air passing through the apparatus during the distillation in vacuum to a rate of only 1 bubble in one to two seconds is rather difficult to maintain in practice, especially during the successive changes in temperature in the system.

The method of A. J. Bailey and R. J. Robinson¹ requires the refluxing of the sample for twelve to thirty-five hours in 0.04 *N* sodium hydroxide solution and titrating the excess alkali with 0.01 *N* hydrochloric acid. This method is applicable to substances which do not possess acidic functions either *per se*, such as lactones, lactams, etc.¹⁵

In addition to sodium hydroxide,^{10, 23} barium hydroxide⁹ and phosphotungstic acid²¹ have been employed as hydrolyzing agents. The acid formed may be determined not only alkalimetrically^{10, 16-19} or iodometrically^{4, 7, 8, 18, 22} but also potentiometrically^{16-19, 23} and by titration with ethanolamine.²¹

Methods involving transesterification in alcoholic solution of the acidic hydrolysis product have been described by K. Freudenberg and co-workers,⁶ and others.¹³

An alkalimetric semi-micro method using alcoholic potassium hydroxide solution as the hydrolyzing agent has been described by E. P. Clark.³ A comprehensive review of the literature on macro acetyl determination methods involving such hydrolyzing agents as sodium, potassium, calcium, barium, and ammonium hydroxides, as well as sulfuric, hydro-

chloric, and hydriodic acid, has been given by H. Meyer.¹⁴ Successful extension of the methods for the determination of *O*- and *N*-acyl groups to include hydroxyl and primary and secondary amino groups by applying exhaustive acetylation of the alcohol or the amine in pyridine, and back titration of the excess acetylating agent, has been reported by a number of investigators.^{2, 5, 20}

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III. DETERMINATION OF GROUPS REACTIVE TO GRIGNARD REAGENT

Principle

The method is based upon quantitative interaction in a closed system of substances containing groups reactive to Grignard reagent with or without the evolution of gaseous hydrocarbons. Thus substances belonging to any of the types of compounds listed below are treated with a known amount of methyl magnesium iodide to yield methane quantitatively. The volume of methane formed is then measured in a suitably constructed methanometer.

Substances yielding one or more moles of methane:

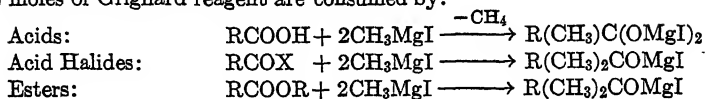
| | | | |
|------------------|----------------------------------|------------------------|-------------------------------------|
| Alcohols: | ROH | + CH ₃ MgI | → CH ₄ |
| Thioalcohols: | RSH | + CH ₃ MgI | → CH ₄ ^{15b} |
| Phenols: | ArOH | + CH ₃ MgI | → CH ₄ |
| Thiophenols: | ArSH | + CH ₃ MgI | → CH ₄ |
| Acids: | RCOOH | + CH ₃ MgI | → CH ₄ |
| | RSO ₂ OH | + CH ₃ MgI | → CH ₄ |
| Amides: | RCONH ₂ | + 2CH ₃ MgI | → 2CH ₄ ^{15b} |
| | RCONHR | + CH ₃ MgI | → CH ₄ ^{15b} |
| Sulfonamides: | RSO ₂ NH ₂ | + 2CH ₃ MgI | → 2CH ₄ |
| | RSO ₂ NHR | + CH ₃ MgI | → CH ₄ |
| Amines: | RNH ₂ | + 2CH ₃ MgI | → 2CH ₄ |
| | R ₂ NH | + CH ₃ MgI | → CH ₄ |
| Nitro compounds: | RNO ₂ | + CH ₃ MgI | → CH ₄ ⁷ |
| Water: | H ₂ O | + 2CH ₃ MgI | → 2CH ₄ ^{3,15b} |

After the evolution of methane due to active hydrogen, the unused Grignard reagent is reacted with a known quantity of aniline and the volume of methane thus generated is again measured. Thus, by difference, such groups as react with methyl magnesium iodide *without* the evolution of methane can be determined by the amount of Grignard reagent consumed, as indicated below:

1 mole of Grignard reagent is consumed by:

| | | | |
|--------------------|--------------------|-----------------------|------------------------------------|
| Aldehydes: | RCHO | + CH ₃ MgI | → RCHOMgI |
| Ketones: | R ₂ CO | + CH ₃ MgI | → R ₂ COMgI |
| Halogen compounds: | RCH ₂ X | + CH ₃ MgI | → RCH ₂ CH ₃ |
| Nitriles: | RCN | + CH ₃ MgI | → RC(CH ₃):NMgI |
| Isonitriles: | RNC | + CH ₃ MgI | → RN:C(CH ₃)MgI |

2 moles of Grignard reagent are consumed by:



Apparatus

The apparatus, which is shown in Fig. 62, consists of two parts: the methane generator and the methanometer. They are connected with a rubber tubing 16 cm. long having a bore of 3 mm. and an outer diameter of 9 mm.

Methane Generator. This part of the apparatus consists of the removable reaction flask (*a*), the two burets (*b*₁ and *b*₂), the Grignard reagent stock flask or reagent vessel (*c*), and two three-way stopcocks, one of which is on the bottom (*S*-*a*) and the other on the top (*S*-*b*). The Grignard reagent stock flask has a capacity of 50 ml. and is provided with a ground-glass stopper and two outlets. The outlet on the top leads to stopcock *S*-*b*. The outlet on the side is a capillary tubing one arm of which extends to the bottom of the Grignard reagent vessel; the other arm leads to buret *b*₂, where it forms an automatic zero-point adjustment. The reaction flask *a*, which has a capacity of 8 ml., is attached by means of a ground-glass joint to a hollow stopper, or head. The capillary inlet tube *d*, which may be connected with either buret *b*₁ or *b*₂, depending upon the position of stopcock *S*-*a*, is sealed to *S*-*a* and extends through the hollow stopper into the reaction flask. Another capillary tubing leads from the hollow stopper up to the right side arm of stopcock *S*-*b*. Buret *b*₂ is graduated to 0.02 ml., and has a capacity of 2 ml.; it serves for the measurement and the introduction of the Grignard reagent. Buret *b*₁ is also graduated to 0.02 ml. but has a capacity of 1 ml. and is used for the introduction of the aniline. An automatic shaking device is connected to the apparatus by means of a wire attached to the capillary inlet tube.

Methanometer. This consists of two parallel gas burets (*b*₃ and *b*₄), each having a capacity of 7 ml.; both are graduated to 0.02 ml. The methane buret *b*₄ carries two three-way stopcocks at its upper end, which facilitate the admittance of methane or dry nitrogen, respectively. Buret *b*₃ is open on the top to permit establishment of equilibrium with the atmospheric pressure. Its curved bottom is sealed to buret *b*₄ and is provided with an outlet which connects both burets by means of a rubber tubing to the mercury leveling bulb, which is suspended from a rack having a pinion adjustment.

Reagents

*Nitrogen*¹¹ should be of 99.9% purity, as used in the manufacture of electric-light bulbs; it is used for the preparation of the Grignard

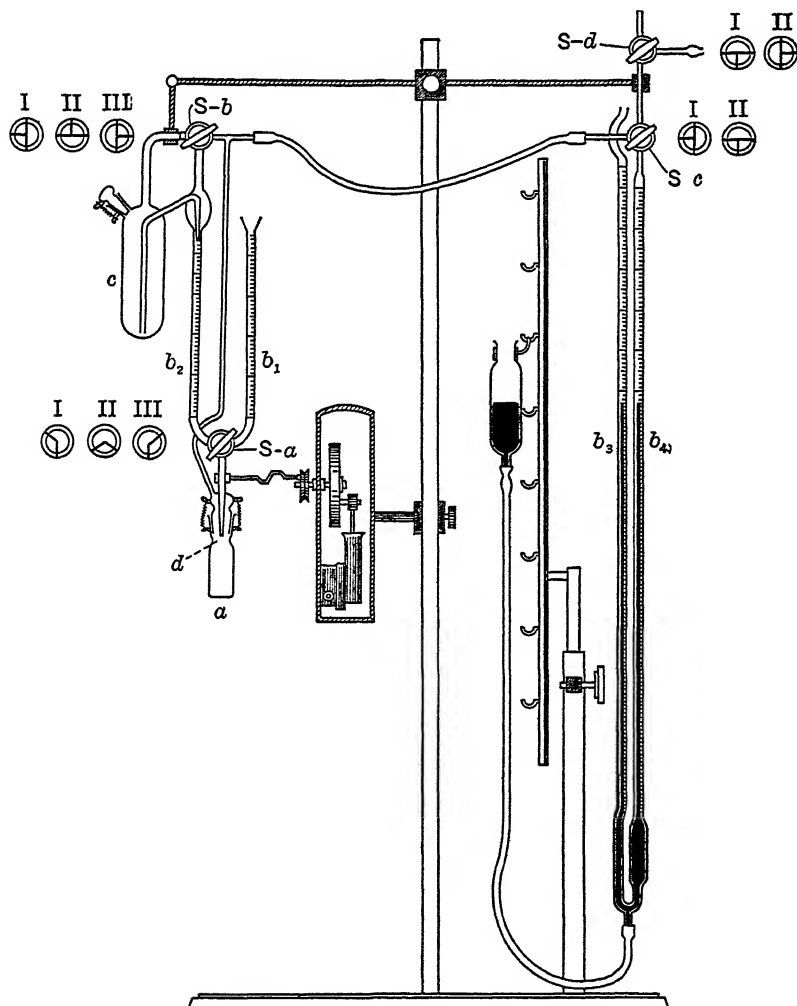


FIG. 62. Apparatus for the Determination of Groups Reactive to Grignard Reagent. Explanation in Text.

reagent as well as during the determination to provide an inert atmosphere. The nitrogen tank should be equipped with a reduction valve

for the regulation of the flow of nitrogen, which is led through a mercury valve bottle, then through a wash bottle containing concentrated sulfuric acid and a U-tube filled with Anhydrone. If it is necessary to purify the nitrogen and free it from oxygen, it is passed over metallic copper heated to about 700° C. and bubbled successively through 50% potassium hydroxide solution and concentrated sulfuric acid.

Solvents

*Anethole*²⁰ is a very good solvent which can readily be purified by distillation (m.p. 22°; b.p. 235°); it is stored in an absolutely dry, ground-glass stoppered reagent bottle over metallic potassium. The best solvent, however, is *pyridine*¹ (b.p. 113–115°). A mixture of pyridine and anethole (1 : 5) is most satisfactory. The pyridine is freed from its homologs by treatment with perchlorate followed by distillation in vacuum. To dry it completely it is placed in a strong, ground-glass-stoppered bottle containing some coarse, freshly ignited barium oxide and shaken for six hours. Then the pyridine is quickly filtered through a fluted filter paper into another ground-glass-stoppered reagent bottle which also contains some freshly ignited barium oxide. After standing for two to three days the pyridine is ready for use.

Amyl ether (b.p. 187–190°) is used as the solvent for the Grignard reagent. It is redistilled and is stored over metallic sodium in a ground-glass-stoppered bottle which has been dried at 100° C.

Grignard Reagent. In a 250-ml. round-bottomed flask are placed 0.6 gram magnesium, 2.5 ml. methyl iodide, and 50 ml. freshly distilled amyl ether. This flask is provided with a ground-glass condenser and a sealed-in inlet tube. The flask is charged through the inlet tube with nitrogen which has been dried by passing it through a wash bottle containing concentrated sulfuric acid and a U-tube filled with Anhydrone. Before the start of the reaction the flow of nitrogen is reduced to about 1 bubble per second. Water is passed through the condenser jacket and, after the reaction has been started by dropping a crystal of iodine into the flask, it is heated for two hours on the water bath. To remove the last traces of methyl iodide the condenser outlet is connected to a suction pump, and the rubber tubing connecting it to the pump is closed with a pinch clamp. The burner is extinguished and the water passing through the condenser jacket shut off, as is the flow of nitrogen. The pinch clamp regulating the vacuum from the suction pump is then slowly opened, causing the contents of the flask to boil which, with the aid of the suction, removes the methyl iodide completely, although a small amount of amyl ether is also lost. As soon as this pinch clamp is fully opened, the pinch clamp beyond the nitrogen inlet

tube is opened to let 1 bubble of nitrogen per second pass through the wash bottle. After fifteen minutes the pinch clamp regulating the vacuum is closed and the one throttling the delivery of nitrogen slowly opened completely so that the flask is again filled with nitrogen. The rubber connections are then removed and the top of the condenser as well as the inlet tube are closed with tight-fitting rubber stoppers or rubber tubings. It is advisable to determine the strength of the reagent before transferring it to the apparatus by dissolving about 5 ml. of the reagent in an excess of 0.1 *N* hydrochloric acid and titrating it back with 0.1 *N* sodium hydroxide. The Grignard reagent should be of 0.4 to 0.5 molar concentration.

Filling the Apparatus with the Grignard Reagent

The apparatus is thoroughly cleaned with dilute hydrochloric acid, water, alcohol, and acetone, and then dried. All grease must be removed from the stopcocks. Stopcocks *S-b*, *S-c*, and *S-d* are greased to transparency, but not excessively, with a vaseline-lanolin mixture. Stopcock *S-a* is lubricated with special stopcock grease, consisting of a mixture of cylinder oil and graphite (1 : 6), but no trace of the lubricant is allowed to enter the bore. The two sections of the apparatus are attached to each other with a good pressure tubing, and the gas burets *b*₃ and *b*₄ are connected to the drying apparatus and valve bottle. Stopcocks *S-a*, *S-b*, *S-c*, and *S-d* are turned to position I, shown in the diagram, and the reaction flask, which is greased sparingly on its upper rim, is attached. Nitrogen is passed through the apparatus for ten minutes at a rate of about 1 bubble per second, and, while nitrogen is still passing through, the Grignard reagent is poured in through the opening of vessel (*c*) with a funnel having a bent stem and a plug of glass wool, in such a manner that the funnel does not run empty until the vessel is filled within 1 cm. of the inlet. A white layer forms on the surface of the reagent, due to the moisture and oxygen absorbed from the air, which, however, is retained by the glass wool. The ground-glass joint of the reagent vessel is also greased sparingly on the upper rim with the vaseline-lanolin mixture. At this stage the Grignard reagent usually shows a slight turbidity which clears up after several hours. Finally, stopcock *S-a* is turned to position III.

Determination of the Blank

Stopcocks *S-b*, *S-c*, and *S-d* are turned to position I and *S-a* to III. With a dry pipet, 0.5 ml. of anethole is introduced into the dry and still warm reaction flask. The upper rim of the flask is greased with the

special stopcock grease and the flask attached to the apparatus. It is placed in a water bath of room temperature, and nitrogen is passed through the apparatus for eight minutes. Buret b_2 is filled with the Grignard reagent by raising the mercury bulb and turning stopcocks $S-a$ and $S-b$ to position II; the buret is filled when the maximum pressure is reached in the reagent vessel, e.g., when nitrogen is escaping from the mercury valve bottle. Stopcock $S-b$ and then $S-a$ are turned counter-clockwise to position III, utilizing the excess pressure to force the reagent into the buret. As soon as the reagent rises beyond the zero point adjustment stopcock $S-b$ is turned to position I, causing the excess to flow back into the reagent vessel. The excess pressure may not be sufficient to force the reagent into the buret if the reagent vessel is completely filled, in which case stopcocks $S-c$ and $S-a$ are turned to position II and the buret filled by lowering the mercury bulb. The excess is again siphoned back into the reagent vessel by raising the mercury bulb. The reagent vessel and buret are shut off from the rest of the apparatus by turning stopcock $S-b$ to position I. Stopcock $S-c$ is turned to I and $S-a$ to III to permit nitrogen to pass through the apparatus for the purpose of temperature equalization. After ten minutes the mercury in gas burets b_3 and b_4 is raised to zero and stopcock $S-c$ and then $S-a$ are turned to position II. The mercury bulb is lowered approximately 10 cm. and stopcock $S-a$ is turned clockwise to position I; 0.5 ml. of Grignard reagent is run from the Grignard buret (b_2) into the reaction flask, and stopcock $S-a$ is turned back to position II. After the reaction flask has been shaken for five minutes, the mercury buret b_3 is raised to zero and burets b_2 and b_4 are read. The difference between b_4 and b_2 represents the blank volume (v_b).

Next, the reaction flask is immersed in boiling water and shaken for ten minutes. To facilitate the release of the gases during this procedure, the mercury bulb is lowered 3 to 4 cm. to create a slight underpressure. The flask is then cooled for ten minutes in water at room temperature, with shaking. The mercury in buret b_3 is raised to zero and b_4 is read again. The blank should show no increase after heating the reagent, except when pyridine is used. This substance does give a higher blank when heated, but since it is also necessary to heat the reaction flask when an unknown substance is analyzed, the blank must be carried out under the same conditions; the blank volume for 0.5 ml. of Grignard reagent should not be higher than 0.2 ml.^{13, 18, 20}

To determine the molarity of the reagent, buret b_1 is filled with aniline and the volume is read accurately. The mercury bulb is lowered about 10 cm.; stopcock $S-a$ is turned to position III and 0.6 to 0.9 ml. of aniline is run in, and $S-a$ is turned to position II and the reaction flask

is shaken for five minutes. The mercury in buret b_3 is then raised to zero and b_4 is read. The amount of reagent and aniline used is deducted from the gas volume in the buret to determine the volume of methane produced by the reagent (v_a). Its strength is expressed in milliliters of methane at 0° C. and 760 mm. pressure per milliliter of reagent, or by its molarity. It is necessary to determine the strength of the reagent only when working with substances which react with the Grignard reagent but do not liberate methane. During the various manipulations of the apparatus it is advisable to touch the gas burets and glass tubings as little as possible.

Procedure

Preparation of the Apparatus. The reaction flask is removed from the apparatus and cleaned with ethyl alcohol and dilute hydrochloric acid; the grease is removed from its neck with cotton wound around a knurled iron wire and moistened with acetone. It is finally rinsed with acetone and dried at 100° C. The ground-glass joint of the reaction flask is also thoroughly cleaned with cotton moistened with acetone. Stopcock $S-a$ is then turned to position III, and some alcohol, and then some acetone, are introduced through buret b_1 . Should there be deposits of magnesium salts in the capillary, they are removed with dilute hydrochloric acid. While the reaction flask and the pipet are permitted to dry in a drying block, a slow stream of nitrogen is passed through the apparatus, with stopcocks $S-d$ and $S-c$ in position I; air is drawn through capillary d at the same time to dry buret b_1 , and after five minutes the apparatus is ready for the determination.

Introduction of the Sample. Enough substance is weighed in the weighing tube to yield about 1 ml. of methane and is transferred to the still warm reaction flask. With the warm pipet 0.5 ml. of anethole, or pyridine, or a mixture of both, is added; then the flask is attached, stopcocks $S-d$, $S-c$, $S-b$ are turned to position I, $S-a$ is turned to position III, and nitrogen is passed through the apparatus. Then the reaction flask is immersed in water at room temperature and shaken to bring about equalization of temperature.

If the substance does not dissolve during the shaking, the reaction flask is heated to 100° C. on the heating block. The substance must not precipitate out upon cooling.

Generation of Methane. After ten minutes, when the temperature has become equalized, buret b_2 is filled with the reagent. The mercury in gas burets b_3 and b_4 is raised to zero and stopcocks $S-c$ and $S-a$ are turned to position II. The mercury bulb is lowered about 10 cm., stopcock $S-a$ is turned clockwise to position I, and about 0.5 ml. of

reagent, or an excess over the theoretical amount, is run into the reaction flask. Then stopcock *S-a* is turned to position II. The reaction flask is shaken at room temperature for five minutes, after which the mercury in buret b_3 is raised to zero and burets b_2 and b_4 are read. The blank volume as well as the amount of reagent added are deducted to obtain the volume of methane formed by the substance. The mercury bulb is lowered again, the reaction flask is then immersed in boiling water, and the shaking is continued for ten minutes. The hot water is then replaced by water at room temperature and the reaction flask shaken for another ten minutes. The mercury in gas buret b_3 is raised to zero and buret b_4 is read.

Addition of Aniline. After completion of the reaction and readings buret b_1 is filled with aniline and read accurately. About 0.7 ml. of aniline is run into the reaction flask by lowering the mercury bulb and turning stopcock *S-a* to position III. Stopcock *S-a* is turned to position II and the reaction flask is shaken for five minutes at room temperature. The mercury in buret b_3 is raised to zero and buret b_4 is read. The volume of aniline added is then deducted from the increased gas volume and the blank added to obtain the volume of methane corresponding to the amount of unused reagent. The time required for the entire analysis, including the weighing of the substance, is about one hour.

Calculation:

Three calculations are involved (see p. 298):

1. The calculation of the volume of methane produced by the sample at room temperature (v_R).
2. The calculation of the volume of methane produced by the sample at elevated temperature (v_T).
3. The calculation of the final volume of methane (v_f).

Remarks

The method for the determination of groups reactive to Grignard reagent as presented in this manual is the method of A. Soltys.²⁰ This method, which is based upon the observations of L. Tschugaeff,²¹ the macromethods of T. Zerewitinoff²² and E. P. Kohler and co-workers,⁸ and the micromethod of B. Flaschenträger,⁴ appears to incorporate all the latest improvements. Specifically, it has the advantage that, in addition to the determination of active hydrogen, it allows the quantitative determination of any other atomic or molecular group or groups capable of reacting with a Grignard reagent.^{2, 5, 7-9, 14, 15a-17, 19}

Gas volumetric methods for the determination of active hydrogen

alone, which consequently involve a simpler apparatus, have been devised by H. Roth,^{15a, 17} W. Fuchs and co-workers,⁵ and others.⁴ The methane evolved may also be determined manometrically¹⁰ as well as gravimetrically in the form of carbon dioxide and water, as demonstrated by R. N. Evans and co-workers.³

Complete solubility of the substance in the solution of the Grignard reagent is absolutely necessary. As solvents, aliphatic (di-*n*-butyl, di-*n*- and isoamyl, etc.) and aromatic ethers (anisole,⁶ anethole,²⁰ etc., as well as aromatic hydrocarbons (xylene,¹⁹ etc.) and pyridine,^{1, 16, 20} have been suggested. The solvents must be perfectly dry, a condition which is not always easy to fulfill. It was found that even metallic sodium is not sufficient, and the use of phosphorus pentoxide in cases of non-reactive solvents had to be resorted to. The sensitivity of the Grignard reagent towards moisture⁶ has been repeatedly employed for the determination of water of crystallization.^{15b} R. N. Evans and co-workers³ utilized this property of Grignard reagents in their gravimetric method for the determination of moisture in insulating materials. Absence of oxygen in the apparatus is highly desirable,^{6, 12} and therefore the use of nitrogen¹¹ in all methods involving Grignard reagents is preferred.

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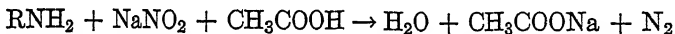
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IV. OTHER METHODS

In addition to the more general structural analytical methods given in the preceding chapters, a number of special methods suitable for more or less specific substances or conditions have been developed.

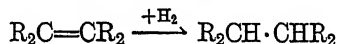
Of these the method of D. D. Van Slyke⁴⁹ for the determination of *primary amines* is one of the most widely used.^{32, 39a, 41a, 42} Primary amines are treated in a closed system with nitrous acid to yield nitrogen, i.e.:



The nitrogen is determined *volumetrically*. The apparatus employed is somewhat similar to the one described in the manometric determination of carbon (p. 140); it consists essentially of the reaction chamber with the graduated dropping funnel, the gas buret, and the Hempel pipet. The solution containing the primary amine is introduced through the graduated dropping funnel into the reaction chamber, which has previously been filled with sodium nitrite solution and acetic acid. The reaction is usually finished in three to five minutes. After purification of the reaction gases by means of the alkaline permanganate solution contained in the Hempel pipet, the volume of the residual nitrogen is determined. A blank is necessary.

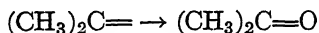
Electrometric and photoelectric methods for the quantitative determination of certain types of organic compounds have come more and more into use. The instruments employed in such procedures have been extensively reviewed by R. H. Müller.^{35, 35a} Conductometric (salts of organic acids),⁴ potentiometric (reducing sugars),³⁷ vitamins,²⁵ photoelectric (hydroxy acids,^{35a, 52} vitamins^{9, 13, 43}), as well as polarographic methods^{19, 26, 36} have been found applicable.

A number of catalytic *micro hydrogenation* methods for the determination of double bonds in organic compounds have been devised.^{3, 12, 21, 28, 51} Platinic oxide and palladium oxides,¹ or platinum black,²⁷ are used as catalysts. The amount of hydrogen consumed may be determined *volumetrically*^{38, 45, 46} or *manometrically*.^{20, 24, 39d, 41d, 48, 50, 53}



In a rather simple all-glass distillation apparatus *isopropylidene groups* may be determined *iodometrically* as acetone.^{2, 5, 7, 8, 11, 14-18, 22,}

23, 29a, 30, 31, 33, 34, 39c, 40, 41c, 47 The acetone is formed either by hydrolysis with 1 *N* sulfuric acid (*O*-isopropylidene groups, acetone sugars, etc.), or by ozonolysis (*C*-isopropylidene groups, unsaturated compounds, etc.). After destruction of interfering by-products by oxidation with 1 *N* potassium permanganate solution, the acetone is converted quantitatively into iodoform by using 2 *N* sodium hydroxide solution and an excess, but known quantity, of 0.05 *N* iodine solution as follows:



The excess iodine is then titrated with 0.05 *N* sodium thiosulfate solution in the usual manner.

By oxidation with chromic-sulfuric acid mixture, and using an apparatus similar to the one employed in the determination of acyl groups (p. 252), *terminal methyl groups* in a number of substances can be oxidized to acetic acid, which is then determined *alkalimetrically*.^{30a, 33, 39b, 41b, 44}

The *optical rotation* of small amounts of optically active substances can be determined by using a micropolarimeter tube and an ordinary polarimeter.^{6, 10, 39e, 41e} Such a micropolarimeter tube is constructed like the conventional tubes, except that the tube itself is a thick opaque glass tube 5 cm. long, 1.4 cm. in outer and 2.5 mm. in inner diameter. The cover glass and the caps are the same as in an ordinary polarimeter tube. The solution is prepared by weighing the substance in the weighing tube and placing it into a suitable stoppered weighing bottle, which is then weighed with the substance and again after the addition of the solvent.

Calculation:

$$[\alpha]_D^t = \frac{100\alpha}{lc}$$

α = observed rotation;

c = concentration of solution (grams of substance in 100 ml. solvent);

l = length of tube in decimeters.

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APPENDIX

I. THE TEACHING OF QUANTITATIVE ORGANIC ELEMENTARY MICROANALYSIS

The methods described in this book can be adapted wholly or in part to form a course in quantitative organic elementary microanalysis. Depending upon the requirements and facilities available, it may be patterned after the course given at New York University, Washington Square College,¹⁹ which is described in this chapter. At New York University it is a graduate course and only students possessing at least a B.Sc. degree, or its equivalent, are accepted. These students have already finished their preliminary studies and possess a fairly uniform average chemical education. Quantitative inorganic analysis is made a prerequisite; no special consideration is given to whether or not the student is majoring in organic or any other branch of chemistry, as it has been found that the training is beneficial for students of any of the experimental sciences, whether physics, biology, or chemistry, because they are made to realize the importance of exactness, cleanliness, and the painstaking following of experimental procedures. Deviations from these requirements certainly will prove fatal to the obtaining of acceptable results, and hence the student gradually acquires what F. Pregl called "chemical asepsis."

The course is given for one term, over a period of fourteen to fifteen weeks; each student is required to reserve one full day a week for the course, and a group of four students comprises the day's class, which makes individual instruction and full supervision readily possible. Each student is assigned his own balance and other apparatus, thereby avoiding interference from other individuals. The balances are alternated; that is, during one period the student uses a microanalytical balance and during the next period an ordinary analytical balance, so that every student is trained in handling and using both types of balances.

The various apparatus, which are permanent set-ups and available in duplicate so that two students can always carry out the same determination independently without interfering with each other, are arranged on tables adjacent to the walls of the room, with the exception of the

two Dumas apparatus, which are on a center table. The equipment furnished each student is simple: it consists of a microspatula, a small camel's-hair brush, a pair each of steel and ivory-tipped forceps, a knurled iron wire, and a wire fork, all of which are kept in a large test tube. In addition, each student is provided with a microdesiccator, which carries the same number as the balance to avoid confusion, a platinum boat, a weighing tube, and a set of weights. The counterpoises for the platinum boat and weighing tube are kept in a small wooden box labeled with the student's name.

Working Schedule. There is a definite assignment of work for every day or period which has to be completed, although an additional day is set aside at the end of the course to permit the student either to make up for lost time or to repeat some of the determinations with which he had the most difficulty. The table below illustrates a typical working schedule for the duration of the term:

| | | |
|--|----|----------------|
| Total number of periods (days)..... | 15 | |
| | | <i>Periods</i> |
| Weighing: Determination of sensitivity and precision; calibration of weights. | | |
| Microanalytical balance (pp. 15-21, 26-30)..... | 1 | |
| Ordinary analytical balance (pp. 23-26, 26-30)..... | 1 | |
| Determination of metals and neutralization equivalent (p. 67)... | 1 | |
| Determination of aminoid nitrogen (Kjeldahl) (pp. 72-74)..... | 1 | |
| Gasometric determination of nitrogen (Dumas) (pp. 89-95)..... | 3 | |
| Determination of carbon and hydrogen (pp. 123-126, 128-132)... | 4 | |
| *Determination of halogen (Carius) (pp. 156-160)..... | 1 | |
| *Determination of sulfur (Carius) (pp. 185-188)..... | 1 | |
| Determination of molecular weight (cryoscopic method) (p. 218). | 1 | |
| Laboratory examination: | | |
| Duplicate carbon and hydrogen analysis and duplicate analyses on same sample for one other element, or molecular-weight determination..... | 1 | |
| Total..... | 15 | |

* Samples are weighed and pressure tubes are filled and sealed the preceding day.

The training period outlined above does not include the setting up of the more complicated apparatus, although the student is given an opportunity to learn how to fill the absorption tubes and the combustion tubes for the Dumas and the carbon and hydrogen apparatus. The student is instructed to perform first duplicate analyses of known substances and then at least one or more duplicate analyses of research compounds. The following minimum accuracy is required:

| KIND OF DETERMINATION | ALLOWABLE ERROR |
|------------------------------------|--------------------|
| Metals..... | $\pm 0.2\%$ |
| Neutralization equivalent..... | $\pm 2.0\%$ |
| Nitrogen (Kjeldahl)..... | $\pm 0.2\%$ |
| Nitrogen (Dumas)..... | $\pm 0.2\%$ |
| Carbon and hydrogen..... | $\pm 0.3\%$ |
| Halogen..... | $\pm 0.3\%$ |
| Sulfur..... | $\pm 0.3\%$ |
| Molecular weight (cryoscopic)..... | $\pm 5.0\%$ |

The various methods are taught by having the instructor demonstrate the first determination of each procedure and then supervise closely while the student carries out the subsequent analyses, until the student has acquired the necessary experience to work independently. To teach the student to utilize his time to the fullest extent, he is compelled to observe strictly the time schedule outlined in the procedure; working by the stopwatch is resorted to in determinations where observance of exact time limits is of importance. At the end of the day the student is required to enter the results obtained in a notebook, which is handed to the instructor, who compares them with the theoretical values. The instructor also keeps a separate permanent record of every analysis made by the student, as well as a record of the sensitivity and precision of the balances before and after the course. For research substances separate reports, signed by the student, are made out which give all the important data pertaining to the analyses.

Examination unknowns are handed out in the last period of the course. They consist of the total analysis of one unknown substance, usually a research compound, requiring, in addition to quantitative carbon and hydrogen determination, at least one, but not more than two, further independent determinations, such as nitrogen, metal, neutralization equivalent, or molecular weight. If time permits, any one of the other standard quantitative microdeterminations, such as alkoxy, may be taken up and practiced.

The course in quantitative organic microanalysis has been given at New York University in the systematic manner outlined above since its incorporation in the curriculum of the Graduate School with the following attendance:

[illegible]

In the table below are shown the average number of the various determinations taught during the course in 1940, which consists of fourteen periods or days of eight hours each, and one period for the laboratory examination at the end of the term.

| KIND OF ANALYSES | TOTAL ANALYSES | KNOWN SUBSTANCES | RESEARCH SUBSTANCES |
|---------------------------|-------------------|---------------------|------------------------|
| Metal | 3 | 2 | 1 |
| Neutralization equivalent | 3 | 2 | 1 |
| Nitrogen (Kjeldahl) | 6 | 3 | 3 |
| Nitrogen (Dumas) | 12 | 4 | 8 |
| Carbon and hydrogen | 18 | 6 | 12 |
| Halogen (Carius) | 4 | 2 | 2 |
| Sulfur (Carius) | 3 | 2 | 1 |
| Molecular weight | 4 | 2 | 2 |
| Total | 53 | 23 | 30 |

During the period from 1934 to 1940 the following number of analyses of both known and research substances were carried out by the 120 students who have taken the course:

| KIND OF ANALYSES | TOTAL ANALYSES | KNOWN SUBSTANCES | RESEARCH SUBSTANCES |
|---------------------------|-------------------|---------------------|------------------------|
| Metal | 639 | 430 | 209 |
| Neutralization equivalent | 762 | 488 | 274 |
| Nitrogen (Kjeldahl) | 871 | 553 | 318 |
| Nitrogen (Dumas) | 1447 | 740 | 707 |
| Carbon and hydrogen | 1729 | 845 | 884 |
| Halogen (Carius) | 296 | 168 | 128 |
| Sulfur (Carius) | 184 | 120 | 64 |
| Molecular weight | 432 | 256 | 176 |
| Total | 6360 | 3600 | 2760 |

From the above figures another important fact may be observed, namely, that a course of this type, aside from its educational value, constitutes a definite asset to any institution pursuing organic chemical research, inasmuch as it affords the analysis of a large number of research substances.

The teaching schedule may be varied to suit individual needs. Thus it may be suitably shortened by either omitting analyses of research substances or by adapting one of the following shortened schedules or by a combination of both.

SHORTENED SCHEDULES

| <i>Periods</i> | <i>A</i> | <i>B</i> |
|-----------------------|-------------------------------|---------------------|
| 1st and 2nd..... | Weighing | Weighing |
| 3rd..... | Determination of metals | Titration |
| 4th..... | Titration | Kjeldahl |
| 5th and 6th..... | Dumas | Dumas |
| 7th, 8th and 9th..... | Carbon and hydrogen | Carbon and hydrogen |
| 10th and 11th..... | Molecular weight (cryoscopic) | Halogen and sulfur |

Remarks

With the introduction of ordinary analytical balances of proper sensitivity and precision in quantitative organic microanalysis²⁰ there appears to be less need than ever to resort to so-called semi-micro-methods,^{9, 14, 16, 23, 24} but the classical quantitative micro procedures of F. Pregl,^{21, 22} F. Emich,^{10, 11} and others^{5, 12, 17, 19, 25} can be taught and practiced under conditions as found in any average quantitative chemical laboratory. A course in organic quantitative microanalysis has, in addition to the often-repeated benefits of a course in micro-technic,^{1-4, 6-10, 13, 15, 18, 23} such advantages as development of "experimental asepsis," saving of time and materials, and this exceptional feature—that it is also of invaluable aid to organic chemical research. At present some fifteen universities and colleges in the United States have a course in quantitative organic microanalysis in their regular teaching curriculum.^{4a}

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II. INSTALLATION OF A LABORATORY FOR QUANTITATIVE ORGANIC ELEMENTARY MICROANALYSIS

General Layout

The general layout of a laboratory for quantitative organic elementary microanalysis intended for industrial use need not differ from one designed for teaching purposes. There are several reports in the literature citing the experiences in the installation of such laboratories.¹⁻²⁰

The laboratory for quantitative organic elementary microanalysis at New York University, Washington Square College, New York City, which is described below, has been in continuous use for teaching as well as research purposes since its installation in 1925.^{3a, 18}

Laboratory. Two rooms are used, which are neither air conditioned, nor possess any dust, humidity, or temperature control. One room, one section of which serves as the balance room, measures $13\frac{1}{2}$ by 29 feet; the other room, in which the various set-ups, with the exception of the Dumas apparatus, are located, is 29 feet long, its front section, which faces the windows, being 23 feet wide.

Balances. Four microanalytical balances (three Kuhlmann and one Starke-Kammerer) varying in sensitivity and precision from ± 1 to ± 3 micrograms, and two ordinary analytical balances (Ainsworth and Becker), possessing a sensitivity and precision of ± 10 micrograms each, are set up on an L-shaped heavy stone table at the wall opposite the window. One section of the L-shaped stone table, which accommodates the two analytical balances and one microbalance, measures $9\frac{1}{2}$ by $21\frac{1}{2}$ feet, and the other section, providing accommodation for four microbalances, measures $13\frac{1}{2}$ by $21\frac{1}{2}$ feet. The only permanent set-up in this room is the double Dumas apparatus which, being near the window of the room, is well away from the balances. In the adjoining room are the double carbon and hydrogen combustion trains, the double Kjeldahl, the molecular-weight, and the halogen and sulfur apparatus. The center table, provided with adequate lighting, is reserved for the titration equipment, that is for the burets containing the various standard solutions. On the three tables flanking the center table, there are, in the front and facing the windows, the double carbon and hydrogen combustion trains, at the right the double Kjeldahl apparatus, and at the left

the molecular-weight and halogen and sulfur apparatus. The free space left is used for the temporary set-ups. The double Dumas apparatus, as mentioned above, is located in the adjacent balance room.

Permanent Set-Ups

Carbon and Hydrogen Apparatus. This requires a table 8 feet in length and 2 feet in width. It can be an ordinary wooden table, but if gas burners are used its top should be of stone, or else asbestos sheets should be placed below the gas burners. The oxygen tank, well secured, is placed either on the side or back of the apparatus, so that it does not obstruct the movements of the operator in any way. For the aspirator, which should be located near the balance, a table 3 feet in length and 2 to 3 feet in width is used.

Kjeldahl Apparatus. A space of about 3 by 2 feet is necessary to accommodate the distillation apparatus and one steamer. Gas as well as water connections and a sink must be available. An additional space of about 2 feet each is required for the digestion stand and the titration outfit. Altogether a table of 7 by 2 feet is required.

Halogen and Sulfur Determination Apparatus. Any one of these apparatus requires a table 3 by 2 feet and an additional 3 by 2 feet for the water bath and filtration. The space where the filtration and drying are carried out is covered preferably with a glass plate. The table for the apparatus itself should have a stone top or be adequately protected from the heat of the burners by a heavy asbestos sheet.

Apparatus for the Molecular-Weight Determinations. None of the methods for the determination of molecular weight requires more than about 2 by 3 feet of table space.

Titration Apparatus. Three standard solutions are required:

- 0.01 *N* acid solution,
- 0.01 *N* sodium hydroxide solution,
- 0.01 *N* sodium thiosulfate solution.

Burets of 10-ml. capacity and calibrated to 0.05 ml. with automatic zero-point adjustment, and provided with protection tubes filled with Ascarite and a suitable automatic filling arrangement, are used. One-liter stand bottles are usually employed.

Total Space. A room 10 by 20 feet will provide sufficient space for the balance and all apparatus, as well as a small office desk. The minimum table space required for single set-ups would be about 34 by 2 feet, distributed as listed below:

- 3 by 2 feet for the balance
- 8 by 2 feet for the carbon and hydrogen apparatus
- 3 by 2 feet for the aspirator
- 6 by 2 feet for the Dumas apparatus
- 5 by 2 feet for the Kjeldahl apparatus
- 3 by 2 feet for the titration equipment
- 3 by 2 feet each for the halogen and sulfur apparatus
- 3 by 2 feet for each apparatus for the molecular weight determination

Temporary Set-Ups

Most of the apparatus employed in the quantitative determination of elements in organic compounds are permanent set-ups. Small or compact apparatus can be easily stored away on the side shelves or in drawers, either in the assembled or dismantled state (determination of metals, molecular weights, alkoxyl, etc.). Some of the apparatus for the determination of atomic or molecular groupings (active hydrogen, etc.) are rather complicated affairs and, if they are used constantly, a permanent set-up is certainly in order.

Cost

In order to find the minimum cost for the installation of the quantitative elementary organic microanalytical methods the catalogs and price lists of several commercial supply houses have been consulted. For single set-ups the prices varied from \$1000 to \$1200. This includes a microanalytical balance of the usual type and the weighing utensils as well as the miscellaneous laboratory utensils, the carbon and hydrogen apparatus, the Dumas and the Kjeldahl apparatus, one complete apparatus for the Carius method for the determination of halogen and sulfur, one each for the molecular-weight determination.

Personnel

The person in charge of a microanalytical laboratory practicing the methods described must not only be able to follow the various procedures, but must also be capable of setting up the various apparatus and of detecting and remedying defects. The taking of a course in quantitative organic elementary microanalysis alone will not suffice for the acquisition of the necessary knowledge. The additional experience required may be gained either by the trial-and-error method by the individual concerned, or by the far easier method of duplicating working set-ups thoroughly tried in a laboratory already adapted to the methods. The person performing the routine analytical work does not have to be a highly trained individual. The paramount requirement in routine

analysis is the orthodox and unswerving following of acknowledged procedures, deviations from which usually end in unsatisfactory analytical results.

Applications and Reports of Analyses

At universities as well as in industrial or academic research organizations it is advisable, in order to save unnecessary work and to facilitate the execution of the analysis, that for every substance to be analyzed an application for analysis be made out which is signed or endorsed by the person in charge of the research. Such an application, as shown below, should state some of the physical and chemical characteristics of the compound. It should also give information in regard to the behavior of the substance upon combustion, that is, whether the compound is explosive, whether it sublimes, or whether it is hygroscopic, or volatile, or very difficult to combust. All these properties of the substance require special attention, and much time is saved by furnishing the analyst with this information, who otherwise may waste an analysis, during the course of which he has to acquaint himself with the behavior of the sample.

APPLICATION FOR ANALYSIS

Name of applicant.....Date.....
Recommended by (director of research).....
Name or number of compound.....
Physical constants of compound:
M.p.:.....B.p.:.....Other constants.....
Criteria for the purity of the compound (state reasons for believing it is pure):
.....
.....
Behavior of compound on heating (state whether the substance distills, sublimes, decomposes, explodes, and whether easy or difficult to combust):
.....
.....
State whether compound is volatile.....hygroscopic.....
Quantitative analysis is desired for the following elements:
Carbon and hydrogen.....Nitrogen.....
Halogen.....Sulfur.....Mol. wt.....
Other determinations.....
(Samples of about 20 mg. in small vials or sealed ampules, well labeled, should be furnished; the samples will not be returned, but are kept for reference.)

Upon completion of the analysis a corresponding report is made out in duplicate by the analyst, one of which is retained by him, giving the weight of the sample, the weight or volume of the combustion products, and, for the carbon and hydrogen determination, a statement whether

or not a residue was observed. A permanent record of all the analyses performed should be kept, because it is often necessary to look up the results of an analysis made months ago. An example of such a report is given below:

REPORT OF ANALYSIS

| | |
|---|-----------------------|
| Name or number of compound..... | Date..... |
| | I II |
| Quantitative carbon and hydrogen determination: | |
| Weight of sample..... | |
| Weight of water..... | |
| Weight of carbon dioxide..... | |
| Percentage of hydrogen..... | |
| Percentage of carbon..... | |
| Quantitative nitrogen determination: | |
| Weight of sample..... | |
| Net volume of nitrogen..... | |
| Temperature and pressure..... | |
| Percentage of nitrogen..... | |
| Other determinations: | |
| Kind of determination..... | |
| Weight of sample..... | |
| Weight of..... | |
| Milliliters of..... | |
| Percentage of..... | |
| Molecular-weight determination: | |
| Ebullioscopic..... | Cryoscopic..... |
| Weight of sample..... | |
| Weight of solvent..... | |
| Depression, elevation..... | |
| Molecular weight..... | |
| Remarks..... | |
| Record book: Date..... | Page..... No..... |
| Analysis performed for..... | |
| Analyst..... | |

It is advisable that upon the receipt of the report the research worker advise the analyst whether the results checked with the expectation, particularly whether they were within the general limits of accuracy of the respective methods involved. The accuracy of the various methods is given in the table on p. 279, and from this table it is evident that no *micro* errors can be expected. Since the reaction laws do not change when the size of the sample is decreased, micromethods cannot generally be expected to give better results than the respective macromethods,

although quite often in the hands of an experienced analyst results within $\pm 0.1\%$ of the theoretical value are obtained, with the exception of the structure analytical, and the molecular-weight methods.

When finer differentiation than the above-mentioned average limits of errors is required, it is by far the wiser procedure to resort to *structure analytical designing* than to demand a higher than usual precision from the analyst. By the introduction of suitable atomic or molecular groupings into the compound (halogen, nitro groups, carboxyl groups, etc.) much finer differentiation is possible than is obtainable by the sole use of analytical methods. The same holds true in the application of any of the structure microanalytical methods (alkoxyl, alkimide, acyl, active hydrogen, etc.). A survey of the literature will bring to light the surprising fact that practically every microanalytical laboratory has its own modifications of such methods. Systematic studies of such methods usually reveal that the procedures given work excellently for the examples cited, but fail, or at least require further modifications and improvements, when used for other types of compounds. With the exception of laboratories where these highly special methods are an absolute necessity and are applied to the same type of substances, it might prove of far greater expediency to resort again to the preparation of suitable derivatives than to force the analyst to set up complicated apparatus and spend one or several weeks in getting satisfactory blanks, only to find out later that the method does not apply to the compounds in question.

In conclusion it can be said that for an average organic research laboratory, even if a great variety of substances belonging to various orders are to be analyzed, the micromethods of quantitative organic elementary analysis given in this book should prove sufficient.

LIST OF CHEMICALS

| | | |
|-------------|------------------|----------------------|
| Acetic acid | Barium | Ethyl alcohol |
| Acetone | chloride | Formic acid |
| Ammonium | hydroxide | Glass cement |
| chloride | oxide | <i>d</i> -Glucose |
| hydroxide | Benzene | Gold chloride |
| iodide | Borneol | Hydrazine sulfate |
| molybdate | Bromine | Hydrochloric acid |
| nitrate | Cadmium sulfate | (sp. gr.: 1.18) |
| sulfate | Camphor | Hydriodic acid |
| Amyl ether | Copper | (sp. gr.: 1.7, 1.96) |
| Anethole | metallic | Iodine |
| Anhydron | oxide, wire | Lead peroxide |
| Aniline | sulfate | Magnesium, metal |
| Asbestos | <i>p</i> -Cymene | Marble |
| Ascarite | Ether | |

| | | |
|---------------------|--------------------------|-------------------------------|
| Mercury | Potassium | Sodium |
| acetate | biiodate | acetate |
| metal | chlorate | bisulfite |
| Methyl red | cyanide | carbonat |
| Nitric acid | dichromate | hydroxide |
| (sp. gr.: 1.42) | hydroxide | metal |
| Nitrogen, tank | iodate | nitrate |
| Oxygen, tank | iodide | peroxide |
| Perhydrol (30%) | metal | thiosulfate |
| Phenol | nitrate | Starch |
| Phenolphthalein | sulfate | Stopcock grease |
| Phosphorus, red | Propionic acid anhydride | Sulfuric acid (sp. gr.: 1.84) |
| Platinized asbestos | Pyridine | p-Toluene sulfonic acid |
| Platinum | Silver | |
| contacts | dichromate | |
| gauze | nitrate | |
| tetrahedrons | wire | |
| wire | wool | |

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III. QUALITATIVE ORGANIC ANALYSIS

In the course of teaching *qualitative organic analysis* for the last thirteen years in the Graduate School of New York University at both the University Heights and the Washington Square branches,^{74, 81a} several attempts have been made to introduce micromethods instead of the conventional macro procedures. It was found that it would not be possible to maintain, for every term, the present working schedule of analyzing seventeen unknowns, including two mixtures of three components each, if micro procedures were used exclusively.

Even though present-day qualitative organic microchemical methods⁸¹ may not lend themselves very readily to routine teaching within the average graduate chemistry curriculum, nevertheless they have a definite place in organic chemical research when small amounts of material are involved. Thus in the following a brief literature survey is presented of present-day microchemical methods for the isolation, purification, and identification of organic compounds.

Isolation and Purification. The microprocedures of isolation and purification^{23, 30e, 105, 109} of organic compounds are usually modeled after the corresponding macro procedures. They comprise *extraction*,^{6, 13, 14a, 20, 22a, 26a, 32, 38, 40, 41, 42, 47, 53, 58, 70-72, 81b, 83, 102, 106, 108, 115} *distillation*,^{8d, 9, 16, 22, 30b, 31c, 33, 43} *sublimation*,^{8e, 16, 30c, 31e, 76a, 97, 101} and *chromatographic* procedures.^{113, 116, 117} For the *crystallization* and *recrystallization* of solids, depending upon the amount of material available, small beakers, test tubes, and centrifuge cones of various sizes, or capillaries, are used.^{1, 9, 31a, b, 86, 91, 97} Instead of filtration,^{68, 86, 90, 91} centrifuging and the use of *porous tiles* is preferable.

*Ordinal Tests.*⁷⁹ The micromethods for the detection of elements in organic compounds^{5, 26, 30f, 31f, 36, 49, 111, 112} include tests for carbon and hydrogen, nitrogen, halogen, sulfur, and other elements. Most useful of these tests is the *micro ammonia* test as devised by F. Emich.^{30f, 31f}

Generic Tests. The literature abounds in the description of microchemical tests with and without the use of a microscope^{1, 4, 7, 30g, j, 31g, 36, 41, 48, 63, 76, 95, 107, 114} for the various types of organic compounds. These methods usually involve color reactions, hydrolysis procedures, or the preparation of suitable derivatives for identification

purposes. In the majority of cases it usually suffices to employ well-known standard macro procedures and tables,^{15, 18, 28, 51, 54, 55, 59, 60, 69, 75, 79, 84, 85, 89, 96, 98, 103, 111} and, depending on the amount of substance available, small distillation flasks and reflux apparatus, test tubes, both open and sealed, centrifuge cones of various sizes, and sealed capillaries have found application.

Determination of Physical Constants. The conventional *melting-point* determination is itself a micro procedure, which may be augmented and refined by using a polarizing microscope with a suitably constructed hot stage.^{8c, 24, 27, 61, 64, 65-67, 86a, 91a, 110, 118} For the determination of the *boiling point* a large variety of methods exists;^{8d, 30b, 31c, 43-45, 49, 76, 82, 86b, 88, 91b, 94, 100} of these, the method of A. Siwoloboff^{79a, 100} appears to be the most practical.

Solubility tests are carried out with centrifuge cones, with capillaries, on microscope slides,^{16b, 62, 95} or by means of *schlieren*. Quite a variety of procedures including the *schlieren* method^{1d, 3, 30l, 31e, 93} have been devised for the determination of the *specific gravity*^{1a, 8a, 10-12, 14, 16a, 17, 19, 21, 25, 30d, 34, 35, 37, 39, 46, 52, 73, 77, 86d, 87, 91d, 104} and the *refractive index*^{1b, c, 2, 8f, 16a, 29, 30a, 56, 57, 62, 65b, 72, 80, 86c, e, 91c, 92, 93, 99, 114} of both liquid and solid organic substances and solutions. Micromethods for the determination of *viscosity*^{8b, 78} and *surface tension* are also known.^{8b}

In addition to the above-cited typical micro procedures, the methods which have been actually used in the isolation, purification, identification, and synthesis of certain rare alkaloids, the hormones, and the vitamins should also be consulted. Thus, in a combination of methods, rather than in the orthodox following of micro procedures alone, lies the solution of many an organic research problem.

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CALCULATIONS

STANDARD FORMULAS

A. GRAVIMETRIC DETERMINATIONS

$$\%E = \frac{\text{wt. } E}{\text{wt. } s} \times 100 \text{ or } \frac{\text{wt. } E \text{ cpd.} \times f_{gr}}{\text{wt. } s} \times 100$$

B. VOLUMETRIC DETERMINATIONS

$$\%E = \frac{\text{ml. std. sol.} \times f_v}{\text{wt. } s} \times 100$$

C. GASOMETRIC DETERMINATIONS

$$\%E = \frac{\text{ml. } v \times f_g}{\text{wt. } s} \times 100$$

$\%E$ = percentage element;

wt. s = weight of sample;

wt. E = weight of element;

wt. E cpd. = weight of element compound (CO_2 ; H_2O ; MeSO_4 ; AgX ; etc.);

ml. std. sol. = ml. standard volumetric solution used in the titration;

ml. v = net volume of E ;

$$f_{gr} \text{ (factor)} = \frac{\text{at. wt. } E}{\text{mol. wt. } E \text{ cpd.}};$$

f_v = equivalent weight of E per 1 ml. standard volumetric solution;

f_g = weight of 1 ml. E at the temperature and pressure of the gas vapors.

A. GRAVIMETRIC DETERMINATIONS

| <i>Type of Determination</i> | <i>Element or Radical</i> | <i>Determined as</i> | <i>Factor</i> | <i>Log of Factor</i> |
|--|--------------------------------|---|---------------|----------------------|
| I. Metals..... | Ba | BaSO ₄ | 0.5883 | 76972 |
| | Ca | CaSO ₄ | 0.2944 | 46894 |
| | K | K ₂ SO ₄ | 0.4487 | 65199 |
| | Na | Na ₂ SO ₄ | 0.3238 | 51025 |
| V. Carbon and hydrogen | C | CO ₂ | 0.2729 | 43600 |
| | H | H ₂ O | 0.1119 | 04875 |
| VI. Halogen..... | Cl | AgCl | 0.2474 | 39340 |
| | Br | AgBr | 0.4255 | 62890 |
| | I | AgI | 0.5405 | 73284 |
| VII. Sulfur | S | BaSO ₄ | 0.1373 | 13782 |
| VIII. Phosphorus..... | P | (MH ₄) ₃ PO ₄ · 12MoO ₃ (empirical) | 0.01453 | 16209 |
| IX. Arsenic..... | As | MgAs ₂ O ₇ | 0.4827 | 68368 |
| ¹ S*—I. Alkoxy and alkimide | OCH ₃ | AgI | 0.1321 | 12096 |
| | OC ₂ H ₅ | AgI | 0.1918 | 28287 |
| | CH ₃ | AgI | 0.06398 | 80604 |
| | C ₂ H ₅ | AgI | 0.12380 | 09273 |

* S = structure analysis.

B. VOLUMETRIC DETERMINATIONS

| Type of Determination | Element or Radical | Standard Solution | Equivalent Weight of 1 ml., mg. | Log of Factor |
|---|--------------------------------|---|---|---------------|
| II. Neutralization equivalent (carboxyl)... | COOH | 0.01 <i>N</i> NaOH | 0.4501 | 65331 |
| III. Aminoid nitrogen... | N | 0.01 <i>N</i> acid | 0.14008 | 14638 |
| VI. Halogens..... | Cl | 0.01 <i>N</i> NaOH | 0.3546 | 54970 |
| | Br | 0.01 <i>N</i> NaOH | 0.7992 | 90263 |
| | I | 0.01 <i>N</i> Na ₂ S ₂ O ₃ | 0.21165 | 32562 |
| VII. Sulfur..... | S | 0.01 <i>N</i> NaOH | 0.1603 | 20493 |
| VIII. Phosphorus..... | P | 0.1 <i>N</i> NaOH | 0.1107 | 04415 |
| IX. Arsenic..... | As | 0.01 <i>N</i> Na ₂ S ₂ O ₃ | 0.3748 | 57380 |
| S—I. Alkoxy and alkimide | OCH ₃ | 0.01 <i>N</i> Na ₂ S ₂ O ₃ | 0.05172 | 71366 |
| | OC ₂ H ₅ | 0.01 <i>N</i> Na ₂ S ₂ O ₃ | 0.07510 | 87564 |
| | CH ₃ | 0.01 <i>N</i> Na ₂ S ₂ O ₃ | 0.02503 | 39863 |
| | C ₂ H ₅ | 0.01 <i>N</i> Na ₂ S ₂ O ₃ | 0.04839 | 68476 |
| S—II. Acetyl..... | CH ₃ CO | 0.01 <i>N</i> Na ₂ S ₂ O ₃ | 0.4302 | 63370 |
| | Benzoyl..... | C ₆ H ₅ CO— | 0.01 <i>N</i> Na ₂ S ₂ O ₃ | 1.0504 |

C. GASOMETRIC DETERMINATIONS

IV. Nitrogen (Dumas method)

ml. v (net volume of nitrogen collected)

Collected ml. of nitrogen (nitrometer reading);

Minus calibration correction (see nitrometer certificate);

Minus air error (determined by blank analysis);

Minus 1.1% of total collected ml. of nitrogen (0.5% for adhesion of the 50% potassium hydroxide solution to the walls, 0.3% for the vapor pressure of the 50% potassium hydroxide solution, 0.3% for the temperature reduction of the barometric reading from room temperature to 0° C.).

S—III. Active Hydrogen

Three separate calculations are necessary: (1) ml. v_t ; (2) ml. v_T ; (3) ml. v_f .

1. ml. $v_t = r_1 - v_r - v_b$.

2. ml. $v_T = r_2 - v_r - v_b$.

3. ml. $v_f = r_3 - r_2 - v_a$.

v_t = volume CH_4 at room temperature (t).

v_T = volume CH_4 at elevated temperature (T).

v_f = volume CH_4 at termination of analysis (final volume).

v_a = volume aniline added (reading of b_1).

v_b = volume CH_4 obtained in the blank test.

v_r = volume of reagent added (reading of b_2).

r_1 = first reading of methane buret (b_4).

r_2 = second reading of methane buret (b_4).

r_3 = third reading of methane buret (b_4).

For the calculation of the net volume of methane, as well as of hydrogen, the nitrogen reduction tables can be used by adding the respective factors:

$$\text{CH}_4 = \frac{22.4}{28} (\log: 90309) \quad \text{H} = \frac{1}{28} (\log: 55673)$$

D. MOLECULAR-WEIGHT DETERMINATIONS

Indirect Methods

(a) From the percentage of element (metals, N, Hal., S, H, etc.):

$$M = \frac{\text{at. wt. } E}{\%E} \times 100$$

(b) From the percentage of a radical ($R = \text{COOH}$, CH_3O , $\text{C}_2\text{H}_5\text{O}$, CH_3CO , etc.):

$$M = \frac{\text{mol. wt. } R}{\%R} \times 100$$

If more than one atom equivalent of the element, or molecular equivalent of the radical (neutral salts of polybasic acids, dimethoxy compounds, etc.), is present, the result is a submultiple of the molecular weight.

(c) From the neutralization equivalent (N.E.):

$$M = \text{N.E.} \times y$$

y = number of free carboxyl groups present.

$$\text{N.E.} = \frac{\text{wt. } s}{\text{ml. std. sol.}}$$

The neutralization equivalent is equal to the molecular weight for a monobasic acid ($y = 1$); otherwise it is a submultiple, from which the molecular weight can be calculated by multiplying the neutralization equivalent with the number of free carboxyl groups present ($\text{N.E.} \times y$).

Direct Methods

(a) Solution methods (ebullioscopic and cryoscopic):

$$M = \frac{C \times \text{wt. } s}{\text{wt. } S \times \Delta}$$

C = constant of solvent (ebullioscopic method; molecular boiling-point elevation constant; cryoscopic method; molecular freezing-point depression constant).

wt. s = weight of sample (solute)

wt. S = weight of the solvent (in the ebullioscopic methods):

wt. S = sp. gr. $\times 1.5$ (Pregl method)

wt. S = sp. gr. $\times 4.0$ (Rieche method)

Δ = observed elevation in boiling point, or observed depression in the melting (or congealing) point of the solvent.

Practical Constants of Liquid Solvents (S)

| | B.pt., °C. | Spec. grav., ²⁰ | ρ 1000 g. | Log of C |
|---------------------------------|------------|----------------------------|-------------------|------------|
| Acetic acid (glacial) | 118.1 | 1.049 | 3.07 | 48714 |
| Acetone | 56.1 | 0.792 | 1.73 | 23805 |
| Benzene | 80.5 | 0.879 | 2.57 | 40993 |
| Chloroform | 61.2 | 1.483 | 3.88 | 58883 |
| Diethyl ether | 34.6 | 0.714 | 2.16 | 23445 |
| Ethyl alcohol | 78.3 | 0.789 | 1.2 | 07918 |
| Water | 100.0 | 0.998 | 0.5 | 69897 |

Practical Constants of Solid Solvents (S)

| | M. pt., °C. | 1000 g. | Log of C |
|----------------------------|-------------|---------|------------|
| Borneol | 206 | 35.8 | 55388 |
| Camphene | 49 | 31.1 | 49276 |
| Camphor | 176 | 40.0 | 60206 |
| Pinene dibromide | 170 | 80.9 | 90795 |

(b) Vaporimetric method:

$$M = 62351 \frac{\text{wt. } s (273.2 + T_2)}{VP}$$

$$V = \frac{g - c_1(T_2 - T_1)}{\quad} - v_s$$

$$P = p_1 + p_2 - p_3 + p$$

wt. s = weight of sample.

V = volume of vapor.

g = weight of displaced mercury.

c_1 = correction for expansion per 1° C.

T_1 = initial temperature, °C.

T_2 = final temperature, °C.

d = density of mercury at T_2 .

vs = volume of the sample $\frac{(\text{weight})}{(\text{density})}$ (approximately 1 cu. mm. per mg.)

P = pressure of vapor.

p_1 = barometer reading.

p_2 = vertical distance in millimeters between the mercury meniscus in the vaporizer and the orifice of the capillary outlet tube.

p_3 = vapor pressure of mercury at T_2 .

p = capillary depression of mercury in outlet tube (+8 mm.); temperature reduction of barometer (−2 mm. at 15° C. − 4 mm. at 32° C.); density reduction of mercury in stem of vaporimeter which is inside of heating chamber (−1 mm. for $T_2 = 100^\circ\text{C}$., −2 mm. for $T_2 = 180^\circ\text{C}$., −3.5 mm. for $T_2 = 320^\circ\text{C}$.).

The net value of p is usually small (about + 0.5% of P), and within the limits of accuracy of this method; therefore, for practical purposes this correction may be omitted.

Practical Constants—Using the High-Temperature Apparatus

Bath liquids: Water (100° C.).

p-Cymene (180° C.).

α -Naphthyl methyl ether (270° C.).

Benzyl benzoate (320° C.).

n-Butyl phthalate.

Mercury constants: d at 100° C.: 13.352 log: 12555

180° C.: 13.160 11926

270° C.: 12.947 11227

320° C.: 12.829 10823

p_3 at 100° C.: 0 mm.

180° C.: 9 mm.

270° C.: 123 mm.

320° C.: 368 mm.

Practical Constants—Using Water as a Heating Bath

Blank test with the apparatus: $B = T_2 - T_1 = (\text{c.g.}, 0.03)$

$$M = 62351 \frac{\text{wt. } 373.2}{VP}$$

$$V = \frac{g - B(100 - T_1)}{13.352}$$

$$P = p_1 + p_2$$

(c) Isothermic method:

$$M = \frac{c \times 10}{m}$$

c = concentration of the sample solution.

m = molarity of the standard solution in isopiestic state with the sample solution.

NITROGEN REDUCTION TABLE *

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=690$ | 691 | 692 | 693 | 694 | t° | $p=695$ | 696 | 697 | 698 | 699 |
|-----------|---------|--------|--------|--------|--------|-----------|---------|--------|--------|--------|--------|
| 10 | 03 946 | 04 009 | 04 072 | 04 135 | 04 197 | 10 | 04 260 | 04 322 | 04 385 | 04 447 | 04 509 |
| 11 | 03 793 | 03 856 | 03 919 | 03 982 | 04 044 | 11 | 04 107 | 04 169 | 04 232 | 04 294 | 04 356 |
| 12 | 03 640 | 03 703 | 03 766 | 03 829 | 03 891 | 12 | 03 954 | 04 016 | 04 079 | 04 141 | 04 203 |
| 13 | 03 488 | 03 551 | 03 614 | 03 677 | 03 739 | 13 | 03 802 | 03 864 | 03 927 | 03 989 | 04 051 |
| 14 | 03 336 | 03 399 | 03 462 | 03 525 | 03 587 | 14 | 03 650 | 03 712 | 03 775 | 03 837 | 03 899 |
| 15 | 03 184 | 03 247 | 03 310 | 03 373 | 03 435 | 15 | 03 498 | 03 560 | 03 623 | 03 685 | 03 747 |
| 16 | 03 033 | 03 096 | 03 159 | 03 222 | 03 284 | 16 | 03 347 | 03 409 | 03 472 | 03 534 | 03 596 |
| 17 | 02 883 | 02 946 | 03 009 | 03 072 | 03 134 | 17 | 03 197 | 03 259 | 03 322 | 03 384 | 03 446 |
| 18 | 02 733 | 02 796 | 02 859 | 02 922 | 02 984 | 18 | 03 047 | 03 109 | 03 172 | 03 234 | 03 296 |
| 19 | 02 584 | 02 647 | 02 710 | 02 773 | 02 835 | 19 | 02 898 | 02 960 | 03 023 | 03 085 | 03 147 |
| 20 | 02 435 | 02 498 | 02 561 | 02 624 | 02 686 | 20 | 02 749 | 02 811 | 02 874 | 02 936 | 02 998 |
| 21 | 02 287 | 02 350 | 02 413 | 02 476 | 02 538 | 21 | 02 601 | 02 663 | 02 726 | 02 788 | 02 850 |
| 22 | 02 139 | 02 202 | 02 265 | 02 328 | 02 390 | 22 | 02 453 | 02 515 | 02 578 | 02 640 | 02 702 |
| 23 | 01 992 | 02 055 | 02 118 | 02 181 | 02 243 | 23 | 02 306 | 02 368 | 02 431 | 02 493 | 02 555 |
| 24 | 01 846 | 01 909 | 01 972 | 02 035 | 02 097 | 24 | 02 160 | 02 222 | 02 285 | 02 347 | 02 409 |
| 25 | 01 700 | 01 763 | 01 826 | 01 889 | 01 951 | 25 | 02 014 | 02 076 | 02 139 | 02 201 | 02 263 |
| 26 | 01 555 | 01 618 | 01 681 | 01 744 | 01 806 | 26 | 01 869 | 01 931 | 01 994 | 02 056 | 02 118 |
| 27 | 01 410 | 01 473 | 01 536 | 01 599 | 01 661 | 27 | 01 724 | 01 786 | 01 849 | 01 911 | 01 973 |
| 28 | 01 266 | 01 329 | 01 392 | 01 455 | 01 517 | 28 | 01 580 | 01 642 | 01 705 | 01 767 | 01 829 |
| 29 | 01 122 | 01 185 | 01 248 | 01 311 | 01 373 | 29 | 01 436 | 01 498 | 01 561 | 01 623 | 01 683 |
| 30 | 00 979 | 01 042 | 01 105 | 01 168 | 01 230 | 30 | 01 293 | 01 355 | 01 418 | 01 480 | 01 540 |
| 31 | 00 836 | 00 899 | 00 962 | 01 025 | 01 087 | 31 | 01 150 | 01 212 | 01 275 | 01 337 | 01 397 |
| 32 | 00 694 | 00 757 | 00 820 | 00 883 | 00 945 | 32 | 01 008 | 01 070 | 01 133 | 01 195 | 01 255 |
| 33 | 00 552 | 00 615 | 00 678 | 00 741 | 00 803 | 33 | 00 866 | 00 928 | 00 991 | 01 053 | 01 113 |
| 34 | 00 411 | 00 474 | 00 537 | 00 600 | 00 662 | 34 | 00 725 | 00 787 | 00 850 | 00 912 | 00 972 |
| 35 | 00 270 | 00 333 | 00 396 | 00 459 | 00 521 | 35 | 00 584 | 00 646 | 00 709 | 00 771 | 00 831 |
| 36 | 00 130 | 00 193 | 00 256 | 00 319 | 00 381 | 36 | 00 444 | 00 506 | 00 569 | 00 631 | 00 691 |

* The logarithms up to and including 24° C. were taken from Küster-Thiel, "Logarithmische Rechentafeln für Chemiker," Berlin and Leipzig, Walter de Gruyter & Co., 1935, and the logarithms from 25° up to and including 36° C. were interpolated.

NITROGEN REDUCTION TABLE—*Continued*

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=700$ | 701 | 702 | 703 | 704 | t° | $p=705$ | 706 | 707 | 708 | 709 |
|-------------|---------|--------|--------|--------|--------|-------------|---------|--------|--------|--------|--------|
| 10 | 04 571 | 04 633 | 04 695 | 04 757 | 04 819 | 10 | 04 880 | 04 942 | 05 003 | 05 065 | 05 126 |
| 11 | 04 418 | 04 480 | 04 542 | 04 604 | 04 666 | 11 | 04 727 | 04 789 | 04 850 | 04 912 | 04 973 |
| 12 | 04 265 | 04 327 | 04 389 | 04 451 | 04 513 | 12 | 04 574 | 04 636 | 04 697 | 04 759 | 04 820 |
| 13 | 04 113 | 04 175 | 04 237 | 04 299 | 04 361 | 13 | 04 422 | 04 484 | 04 545 | 04 607 | 04 668 |
| 14 | 03 961 | 04 023 | 04 085 | 04 147 | 04 209 | 14 | 04 270 | 04 332 | 04 393 | 04 455 | 04 516 |
| 15 | 03 809 | 03 871 | 03 933 | 03 995 | 04 057 | 15 | 04 118 | 04 180 | 04 241 | 04 303 | 04 364 |
| 16 | 03 658 | 03 720 | 03 782 | 03 844 | 03 906 | 16 | 03 967 | 04 029 | 04 090 | 04 152 | 04 213 |
| 17 | 03 508 | 03 570 | 03 632 | 03 694 | 03 756 | 17 | 03 817 | 03 879 | 03 940 | 04 002 | 04 063 |
| 18 | 03 358 | 03 420 | 03 482 | 03 544 | 03 606 | 18 | 03 667 | 03 729 | 03 790 | 03 852 | 03 913 |
| 19 | 03 209 | 03 271 | 03 333 | 03 395 | 03 457 | 19 | 03 518 | 03 580 | 03 641 | 03 703 | 03 764 |
| 20 | 03 060 | 03 122 | 03 184 | 03 246 | 03 308 | 20 | 03 369 | 03 431 | 03 492 | 03 554 | 03 615 |
| 21 | 02 912 | 02 974 | 03 036 | 03 098 | 03 160 | 21 | 03 221 | 03 283 | 03 344 | 03 406 | 03 467 |
| 22 | 02 764 | 02 826 | 02 888 | 02 950 | 03 012 | 22 | 03 073 | 03 135 | 03 196 | 03 258 | 03 319 |
| 23 | 02 617 | 02 679 | 02 741 | 02 803 | 02 865 | 23 | 02 926 | 02 988 | 03 049 | 03 111 | 03 172 |
| 24 | 02 471 | 02 533 | 02 595 | 02 657 | 02 719 | 24 | 02 780 | 02 842 | 02 903 | 02 965 | 03 026 |
| 25 | 02 325 | 02 387 | 02 449 | 02 511 | 02 573 | 25 | 02 634 | 02 696 | 02 757 | 02 819 | 02 880 |
| 26 | 02 180 | 02 242 | 02 304 | 02 366 | 02 428 | 26 | 02 489 | 02 551 | 02 612 | 02 674 | 02 735 |
| 27 | 02 035 | 02 097 | 02 159 | 02 221 | 02 283 | 27 | 02 344 | 02 406 | 02 467 | 02 529 | 02 590 |
| 28 | 01 891 | 01 953 | 02 015 | 02 077 | 02 139 | 28 | 02 200 | 02 262 | 02 323 | 02 385 | 02 446 |
| 29 | 01 747 | 01 809 | 01 871 | 01 933 | 01 995 | 29 | 02 056 | 02 118 | 02 179 | 02 241 | 02 302 |
| 30 | 01 604 | 01 666 | 01 728 | 01 790 | 01 852 | 30 | 01 913 | 01 975 | 02 036 | 02 098 | 02 159 |
| 31 | 01 461 | 01 523 | 01 585 | 01 647 | 01 709 | 31 | 01 770 | 01 832 | 01 893 | 01 955 | 02 016 |
| 32 | 01 319 | 01 381 | 01 443 | 01 505 | 01 567 | 32 | 01 628 | 01 690 | 01 751 | 01 813 | 01 874 |
| 33 | 01 177 | 01 239 | 01 301 | 01 363 | 01 425 | 33 | 01 486 | 01 548 | 01 609 | 01 671 | 01 732 |
| 34 | 01 036 | 01 098 | 01 160 | 01 222 | 01 284 | 34 | 01 345 | 01 407 | 01 468 | 01 530 | 01 591 |
| 35 | 00 895 | 00 957 | 01 019 | 01 081 | 01 143 | 35 | 01 205 | 01 267 | 01 327 | 01 389 | 01 450 |
| 36 | 00 755 | 00 817 | 00 879 | 00 941 | 01 003 | 36 | 01 065 | 01 127 | 01 187 | 01 249 | 01 310 |

NITROGEN REDUCTION TABLE—*Continued*

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=710$ | 711 | 712 | 713 | 714 | t° | $p=715$ | 716 | 717 | 718 | 719 |
|-------------|---------|--------|--------|--------|--------|-------------|---------|--------|--------|--------|--------|
| 10 | 05 189 | 05 250 | 05 311 | 05 372 | 05 433 | 10 | 05 494 | 05 554 | 05 615 | 05 675 | 05 736 |
| 11 | 05 035 | 05 096 | 05 157 | 05 218 | 05 279 | 11 | 05 340 | 05 400 | 05 461 | 05 521 | 05 582 |
| 12 | 04 882 | 04 943 | 05 004 | 05 065 | 05 126 | 12 | 05 187 | 05 247 | 05 308 | 05 368 | 05 429 |
| 13 | 04 730 | 04 791 | 04 852 | 04 913 | 04 974 | 13 | 05 035 | 05 095 | 05 156 | 05 216 | 05 277 |
| 14 | 04 578 | 04 639 | 04 700 | 04 761 | 04 822 | 14 | 04 883 | 04 943 | 05 004 | 05 064 | 05 125 |
| 15 | 04 427 | 04 488 | 04 549 | 04 610 | 04 671 | 15 | 04 732 | 04 792 | 04 853 | 04 913 | 04 974 |
| 16 | 04 276 | 04 337 | 04 398 | 04 459 | 04 520 | 16 | 04 581 | 04 641 | 04 702 | 04 762 | 04 823 |
| 17 | 04 126 | 04 187 | 04 248 | 04 309 | 04 370 | 17 | 04 431 | 04 491 | 04 552 | 04 612 | 04 673 |
| 18 | 03 976 | 04 037 | 04 098 | 04 159 | 04 220 | 18 | 04 281 | 04 341 | 04 402 | 04 462 | 04 523 |
| 19 | 03 827 | 03 888 | 03 949 | 04 010 | 04 071 | 19 | 04 132 | 04 192 | 04 253 | 04 313 | 04 374 |
| 20 | 03 678 | 03 739 | 03 800 | 03 861 | 03 922 | 20 | 03 983 | 04 043 | 04 104 | 04 164 | 04 225 |
| 21 | 03 530 | 03 591 | 03 652 | 03 713 | 03 774 | 21 | 03 835 | 03 895 | 03 956 | 04 016 | 04 077 |
| 22 | 03 382 | 03 443 | 03 504 | 03 565 | 03 626 | 22 | 03 687 | 03 747 | 03 808 | 03 868 | 03 929 |
| 23 | 03 235 | 03 296 | 03 357 | 03 418 | 03 479 | 23 | 03 540 | 03 600 | 03 661 | 03 721 | 03 782 |
| 24 | 03 088 | 03 149 | 03 210 | 03 271 | 03 332 | 24 | 03 393 | 03 453 | 03 514 | 03 574 | 03 635 |
| 25 | 02 942 | 03 003 | 03 064 | 03 125 | 03 186 | 25 | 03 247 | 03 307 | 03 368 | 03 428 | 03 489 |
| 26 | 02 797 | 02 858 | 02 919 | 02 980 | 03 041 | 26 | 03 102 | 03 162 | 03 223 | 03 283 | 03 344 |
| 27 | 02 652 | 02 713 | 02 774 | 02 835 | 02 896 | 27 | 02 957 | 03 017 | 03 078 | 03 138 | 03 199 |
| 28 | 02 508 | 02 569 | 02 630 | 02 691 | 02 752 | 28 | 02 813 | 02 873 | 02 934 | 02 994 | 03 055 |
| 29 | 02 364 | 02 425 | 02 486 | 02 547 | 02 608 | 29 | 02 669 | 02 729 | 02 790 | 02 850 | 02 911 |
| 30 | 02 221 | 02 282 | 02 343 | 02 404 | 02 465 | 30 | 02 526 | 02 586 | 02 647 | 02 707 | 02 768 |
| 31 | 02 078 | 02 139 | 02 203 | 02 261 | 02 322 | 31 | 02 383 | 02 443 | 02 504 | 02 564 | 02 625 |
| 32 | 01 936 | 01 997 | 02 061 | 02 119 | 02 180 | 32 | 02 241 | 02 301 | 02 362 | 02 422 | 02 483 |
| 33 | 01 794 | 01 855 | 01 919 | 01 977 | 02 038 | 33 | 02 099 | 02 159 | 02 220 | 02 280 | 02 341 |
| 34 | 01 653 | 01 714 | 01 778 | 01 836 | 01 897 | 34 | 01 958 | 02 018 | 02 079 | 02 139 | 02 200 |
| 35 | 01 512 | 01 573 | 01 637 | 01 695 | 01 756 | 35 | 01 817 | 01 877 | 01 938 | 01 998 | 02 059 |
| 36 | 01 372 | 01 433 | 01 497 | 01 555 | 01 616 | 36 | 01 677 | 01 737 | 01 798 | 01 858 | 01 919 |

NITROGEN REDUCTION TABLE—*Continued*

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=720$ | 721 | 722 | 723 | 724 | t° | $p=725$ | 726 | 727 | 728 | 729 |
|-------------|---------|--------|--------|--------|--------|-------------|---------|--------|--------|--------|--------|
| 10 | 05 796 | 05 857 | 05 917 | 05 977 | 06 037 | 10 | 06 097 | 06 157 | 06 216 | 06 276 | 06 336 |
| 11 | 05 642 | 05 703 | 05 763 | 05 823 | 05 883 | 11 | 05 943 | 06 003 | 06 062 | 06 122 | 06 182 |
| 12 | 05 489 | 05 550 | 05 610 | 05 670 | 05 730 | 12 | 05 790 | 05 850 | 05 909 | 05 969 | 06 029 |
| 13 | 05 337 | 05 398 | 05 458 | 05 518 | 05 578 | 13 | 05 638 | 05 698 | 05 757 | 05 817 | 05 877 |
| 14 | 05 185 | 05 246 | 05 306 | 05 366 | 05 426 | 14 | 05 486 | 05 546 | 05 605 | 05 665 | 05 725 |
| 15 | 05 034 | 05 095 | 05 155 | 05 215 | 05 275 | 15 | 05 335 | 05 395 | 05 454 | 05 514 | 05 574 |
| 16 | 04 883 | 04 944 | 05 004 | 05 064 | 05 124 | 16 | 05 184 | 05 244 | 05 303 | 05 363 | 05 423 |
| 17 | 04 733 | 04 794 | 04 854 | 04 914 | 04 974 | 17 | 05 034 | 05 094 | 05 153 | 05 213 | 05 273 |
| 18 | 04 583 | 04 644 | 04 704 | 04 764 | 04 824 | 18 | 04 884 | 04 944 | 05 003 | 05 063 | 05 123 |
| 19 | 04 434 | 04 495 | 04 555 | 04 615 | 04 675 | 19 | 04 735 | 04 795 | 04 854 | 04 914 | 04 974 |
| 20 | 04 285 | 04 346 | 04 406 | 04 466 | 04 526 | 20 | 04 586 | 04 646 | 04 705 | 04 765 | 04 825 |
| 21 | 04 137 | 04 198 | 04 258 | 04 318 | 04 378 | 21 | 04 438 | 04 498 | 04 557 | 04 617 | 04 677 |
| 22 | 03 989 | 04 050 | 04 110 | 04 170 | 04 230 | 22 | 04 290 | 04 350 | 04 409 | 04 469 | 04 529 |
| 23 | 03 842 | 03 903 | 03 963 | 04 023 | 04 083 | 23 | 04 143 | 04 203 | 04 262 | 04 322 | 04 382 |
| 24 | 03 695 | 03 756 | 03 816 | 03 876 | 03 936 | 24 | 03 996 | 04 056 | 04 115 | 04 175 | 04 235 |
| 25 | 03 549 | 03 610 | 03 670 | 03 730 | 03 790 | 25 | 03 850 | 03 910 | 03 969 | 04 029 | 04 089 |
| 26 | 03 404 | 03 465 | 03 525 | 03 585 | 03 645 | 26 | 03 705 | 03 765 | 03 824 | 03 884 | 03 944 |
| 27 | 03 259 | 03 320 | 03 380 | 03 440 | 03 500 | 27 | 03 560 | 03 620 | 03 679 | 03 739 | 03 799 |
| 28 | 03 115 | 03 176 | 03 236 | 03 296 | 03 356 | 28 | 03 416 | 03 476 | 03 535 | 03 595 | 03 655 |
| 29 | 02 971 | 03 032 | 03 092 | 03 152 | 03 212 | 29 | 03 272 | 03 332 | 03 391 | 03 451 | 03 511 |
| 30 | 02 828 | 02 889 | 02 949 | 03 009 | 03 069 | 30 | 03 129 | 03 189 | 03 248 | 03 308 | 03 368 |
| 31 | 02 685 | 02 746 | 02 806 | 02 866 | 02 926 | 31 | 02 986 | 03 046 | 03 105 | 03 165 | 03 225 |
| 32 | 02 543 | 02 604 | 02 664 | 02 724 | 02 784 | 32 | 02 844 | 02 904 | 02 963 | 03 023 | 03 083 |
| 33 | 02 401 | 02 462 | 02 522 | 02 582 | 02 642 | 33 | 02 702 | 02 762 | 02 821 | 02 881 | 02 941 |
| 34 | 02 260 | 02 321 | 02 381 | 02 441 | 02 501 | 34 | 02 561 | 02 621 | 02 680 | 02 740 | 02 800 |
| 35 | 02 119 | 02 180 | 02 240 | 02 300 | 02 360 | 35 | 02 420 | 02 480 | 02 539 | 02 599 | 02 659 |
| 36 | 01 979 | 02 040 | 02 100 | 02 160 | 02 220 | 36 | 02 280 | 02 340 | 02 399 | 02 459 | 02 519 |

NITROGEN REDUCTION TABLE—*Continued*

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=730$ | 731 | 732 | 733 | 734 | t° | $p=735$ | 736 | 737 | 738 | 739 |
|-----------|---------|--------|--------|--------|--------|-----------|---------|--------|--------|--------|--------|
| 10 | 06 395 | 06 455 | 06 514 | 06 573 | 06 633 | 10 | 06 692 | 06 751 | 06 810 | 06 869 | 06 927 |
| 11 | 06 241 | 06 301 | 06 360 | 06 419 | 06 479 | 11 | 06 538 | 06 597 | 06 656 | 06 715 | 06 773 |
| 12 | 06 088 | 06 148 | 06 207 | 06 266 | 06 326 | 12 | 06 385 | 06 444 | 06 503 | 06 562 | 06 620 |
| 13 | 05 936 | 05 996 | 06 055 | 06 114 | 06 174 | 13 | 06 233 | 06 292 | 06 351 | 06 410 | 06 468 |
| 14 | 05 784 | 05 844 | 05 903 | 05 962 | 06 022 | 14 | 06 081 | 06 140 | 06 199 | 06 258 | 06 316 |
| 15 | 05 633 | 05 693 | 05 752 | 05 811 | 05 871 | 15 | 05 930 | 05 989 | 06 048 | 06 107 | 06 165 |
| 16 | 05 482 | 05 542 | 05 601 | 05 660 | 05 720 | 16 | 05 779 | 05 838 | 05 897 | 05 956 | 06 014 |
| 17 | 05 332 | 05 392 | 05 451 | 05 510 | 05 570 | 17 | 05 629 | 05 688 | 05 747 | 05 806 | 05 864 |
| 18 | 05 182 | 05 242 | 05 301 | 05 360 | 05 420 | 18 | 05 479 | 05 538 | 05 597 | 05 656 | 05 714 |
| 19 | 05 033 | 05 093 | 05 152 | 05 211 | 05 271 | 19 | 05 330 | 05 389 | 05 448 | 05 507 | 05 565 |
| 20 | 04 884 | 04 944 | 05 003 | 05 062 | 05 122 | 20 | 05 181 | 05 240 | 05 299 | 05 358 | 05 416 |
| 21 | 04 736 | 04 796 | 04 855 | 04 914 | 04 974 | 21 | 05 033 | 05 092 | 05 151 | 05 210 | 05 268 |
| 22 | 04 588 | 04 648 | 04 707 | 04 766 | 04 826 | 22 | 04 885 | 04 944 | 05 003 | 05 062 | 05 120 |
| 23 | 04 441 | 04 501 | 04 560 | 04 619 | 04 679 | 23 | 04 738 | 04 797 | 04 856 | 04 915 | 04 973 |
| 24 | 04 294 | 04 354 | 04 413 | 04 472 | 04 532 | 24 | 04 591 | 04 650 | 04 709 | 04 768 | 04 826 |
| 25 | 04 148 | 04 208 | 04 267 | 04 326 | 04 386 | 25 | 04 445 | 04 504 | 04 563 | 04 622 | 04 680 |
| 26 | 04 003 | 04 063 | 04 122 | 04 181 | 04 241 | 26 | 04 300 | 04 359 | 04 418 | 04 477 | 04 535 |
| 27 | 03 858 | 03 918 | 03 977 | 04 036 | 04 096 | 27 | 04 155 | 04 214 | 04 273 | 04 332 | 04 390 |
| 28 | 03 714 | 03 774 | 03 833 | 03 892 | 03 952 | 28 | 04 011 | 04 070 | 04 129 | 04 188 | 04 246 |
| 29 | 03 570 | 03 630 | 03 689 | 03 748 | 03 808 | 29 | 03 867 | 03 926 | 03 985 | 04 044 | 04 102 |
| 30 | 03 427 | 03 487 | 03 546 | 03 605 | 03 665 | 30 | 03 724 | 03 783 | 03 842 | 03 901 | 03 959 |
| 31 | 03 284 | 03 344 | 03 403 | 03 462 | 03 522 | 31 | 03 581 | 03 640 | 03 699 | 03 758 | 03 816 |
| 32 | 03 142 | 03 202 | 03 261 | 03 320 | 03 380 | 32 | 03 439 | 03 498 | 03 557 | 03 616 | 03 674 |
| 33 | 03 000 | 03 060 | 03 119 | 03 178 | 03 238 | 33 | 03 297 | 03 356 | 03 415 | 03 474 | 03 532 |
| 34 | 02 859 | 02 919 | 02 978 | 03 037 | 03 097 | 34 | 03 156 | 03 215 | 03 274 | 03 333 | 03 391 |
| 35 | 02 718 | 02 778 | 02 837 | 02 896 | 02 956 | 35 | 03 015 | 03 074 | 03 133 | 03 192 | 03 250 |
| 36 | 02 578 | 02 638 | 02 697 | 02 756 | 02 816 | 36 | 02 875 | 02 934 | 02 993 | 03 052 | 03 110 |

NITROGEN REDUCTION TABLE—*Continued*

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=740$ | 741 | 742 | 743 | 744 | t° | $p=745$ | 746 | 747 | 748 | 749 |
|-------------|---------|--------|--------|--------|--------|-------------|---------|--------|--------|--------|--------|
| 10 | 06 986 | 07 045 | 07 103 | 07 162 | 07 220 | 10 | 07 279 | 07 337 | 07 395 | 07 453 | 07 511 |
| 11 | 06 832 | 06 891 | 06 949 | 07 008 | 07 066 | 11 | 07 125 | 07 183 | 07 241 | 07 299 | 07 357 |
| 12 | 06 679 | 06 738 | 06 796 | 06 855 | 06 913 | 12 | 06 972 | 07 030 | 07 088 | 07 146 | 07 204 |
| 13 | 06 527 | 06 586 | 06 644 | 06 703 | 06 761 | 13 | 06 820 | 06 878 | 06 936 | 06 994 | 07 052 |
| 14 | 06 375 | 06 434 | 06 492 | 06 551 | 06 609 | 14 | 06 668 | 06 726 | 06 784 | 06 842 | 06 900 |
| 15 | 06 224 | 06 283 | 06 341 | 06 400 | 06 458 | 15 | 06 517 | 06 575 | 06 633 | 06 691 | 06 749 |
| 16 | 06 073 | 06 132 | 06 190 | 06 249 | 06 307 | 16 | 06 366 | 06 424 | 06 482 | 06 540 | 06 598 |
| 17 | 05 923 | 05 982 | 06 040 | 06 099 | 06 157 | 17 | 06 216 | 06 274 | 06 332 | 06 390 | 06 448 |
| 18 | 05 773 | 05 832 | 05 890 | 05 949 | 06 007 | 18 | 06 066 | 06 124 | 06 182 | 06 240 | 06 298 |
| 19 | 05 624 | 05 683 | 05 741 | 05 800 | 05 858 | 19 | 05 917 | 05 975 | 06 033 | 06 091 | 06 149 |
| 20 | 05 475 | 05 534 | 05 592 | 05 651 | 05 709 | 20 | 05 768 | 05 826 | 05 884 | 05 942 | 06 000 |
| 21 | 05 327 | 05 386 | 05 444 | 05 503 | 05 561 | 21 | 05 620 | 05 678 | 05 736 | 05 794 | 05 852 |
| 22 | 05 179 | 05 238 | 05 296 | 05 355 | 05 413 | 22 | 05 472 | 05 530 | 05 588 | 05 646 | 05 704 |
| 23 | 05 032 | 05 091 | 05 149 | 05 208 | 05 266 | 23 | 05 325 | 05 383 | 05 441 | 05 499 | 05 557 |
| 24 | 04 885 | 04 944 | 05 002 | 05 061 | 05 119 | 24 | 05 178 | 05 236 | 05 294 | 05 352 | 05 410 |
| 25 | 04 739 | 04 798 | 04 856 | 04 915 | 04 973 | 25 | 05 032 | 05 090 | 05 148 | 05 206 | 05 264 |
| 26 | 04 594 | 04 653 | 04 711 | 04 770 | 04 828 | 26 | 04 887 | 04 945 | 05 003 | 05 061 | 05 119 |
| 27 | 04 449 | 04 508 | 04 566 | 04 625 | 04 683 | 27 | 04 742 | 04 800 | 04 858 | 04 916 | 04 974 |
| 28 | 04 305 | 04 364 | 04 422 | 04 481 | 04 539 | 28 | 04 598 | 04 656 | 04 714 | 04 772 | 04 830 |
| 29 | 04 161 | 04 220 | 04 278 | 04 337 | 04 395 | 29 | 04 454 | 04 512 | 04 570 | 04 628 | 04 686 |
| 30 | 04 018 | 04 078 | 04 135 | 04 194 | 04 252 | 30 | 04 311 | 04 369 | 04 428 | 04 485 | 04 543 |
| 31 | 03 875 | 03 935 | 03 992 | 04 051 | 04 109 | 31 | 04 168 | 04 226 | 04 285 | 04 342 | 04 400 |
| 32 | 03 733 | 03 793 | 03 850 | 03 909 | 03 967 | 32 | 04 026 | 04 084 | 04 143 | 04 200 | 04 258 |
| 33 | 03 591 | 03 651 | 03 708 | 03 767 | 03 825 | 33 | 03 884 | 03 942 | 04 001 | 04 058 | 04 116 |
| 34 | 03 450 | 03 510 | 03 567 | 03 626 | 03 684 | 34 | 03 743 | 03 801 | 03 860 | 03 917 | 03 975 |
| 35 | 03 309 | 03 369 | 03 426 | 03 485 | 03 543 | 35 | 03 602 | 03 660 | 03 719 | 03 776 | 03 834 |
| 36 | 03 169 | 03 229 | 03 286 | 03 345 | 03 403 | 36 | 03 462 | 03 520 | 03 579 | 03 636 | 03 694 |

NITROGEN REDUCTION TABLE—*Continued*

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=750$ | 751 | 752 | 753 | 754 | t° | $p=755$ | 756 | 757 | 758 | 759 |
|-------------|---------|--------|--------|--------|--------|-------------|---------|--------|--------|--------|--------|
| 10 | 07 569 | 07 627 | 07 685 | 07 742 | 07 800 | 10 | 07 858 | 07 915 | 07 973 | 08 030 | 08 087 |
| 11 | 07 415 | 07 473 | 07 531 | 07 588 | 07 646 | 11 | 07 704 | 07 761 | 07 819 | 07 876 | 07 933 |
| 12 | 07 262 | 07 320 | 07 378 | 07 435 | 07 493 | 12 | 07 551 | 07 608 | 07 666 | 07 723 | 07 780 |
| 13 | 07 110 | 07 168 | 07 226 | 07 283 | 07 341 | 13 | 07 399 | 07 456 | 07 514 | 07 571 | 07 628 |
| 14 | 06 958 | 07 016 | 07 074 | 07 131 | 07 189 | 14 | 07 247 | 07 304 | 07 362 | 07 419 | 07 476 |
| 15 | 06 807 | 06 865 | 06 923 | 06 980 | 07 038 | 15 | 07 096 | 07 153 | 07 211 | 07 268 | 07 325 |
| 16 | 06 656 | 06 714 | 06 772 | 06 829 | 06 887 | 16 | 06 945 | 07 002 | 07 060 | 07 117 | 07 174 |
| 17 | 06 506 | 06 564 | 06 622 | 06 679 | 06 737 | 17 | 06 795 | 06 852 | 06 910 | 06 967 | 07 024 |
| 18 | 06 356 | 06 414 | 06 472 | 06 529 | 06 587 | 18 | 06 645 | 06 702 | 06 760 | 06 817 | 06 874 |
| 19 | 06 207 | 06 265 | 06 323 | 06 380 | 06 438 | 19 | 06 496 | 06 553 | 06 611 | 06 668 | 06 725 |
| 20 | 06 058 | 06 116 | 06 174 | 06 231 | 06 289 | 20 | 06 347 | 06 404 | 06 462 | 06 519 | 06 576 |
| 21 | 05 910 | 05 968 | 06 026 | 06 083 | 06 141 | 21 | 06 199 | 06 256 | 06 314 | 06 371 | 06 428 |
| 22 | 05 762 | 05 820 | 05 878 | 05 935 | 05 993 | 22 | 06 051 | 06 108 | 06 166 | 06 223 | 06 280 |
| 23 | 05 615 | 05 673 | 05 731 | 05 788 | 05 846 | 23 | 05 904 | 05 961 | 06 019 | 06 076 | 06 133 |
| 24 | 05 468 | 05 526 | 05 584 | 05 641 | 05 699 | 24 | 05 757 | 05 814 | 05 872 | 05 929 | 05 986 |
| 25 | 05 322 | 05 380 | 05 438 | 05 495 | 05 553 | 25 | 05 611 | 05 668 | 05 726 | 05 783 | 05 840 |
| 26 | 05 177 | 05 235 | 05 293 | 05 350 | 05 408 | 26 | 05 466 | 05 523 | 05 581 | 05 638 | 05 695 |
| 27 | 05 032 | 05 090 | 05 148 | 05 205 | 05 263 | 27 | 05 321 | 05 378 | 05 436 | 05 493 | 05 550 |
| 28 | 04 888 | 04 946 | 05 004 | 05 061 | 05 119 | 28 | 05 177 | 05 234 | 05 292 | 05 349 | 05 406 |
| 29 | 04 744 | 04 802 | 04 860 | 04 917 | 04 975 | 29 | 05 033 | 05 090 | 05 148 | 05 205 | 05 262 |
| 30 | 04 601 | 04 659 | 04 717 | 04 774 | 04 832 | 30 | 04 890 | 04 947 | 05 005 | 05 062 | 05 119 |
| 31 | 04 458 | 04 516 | 04 574 | 04 631 | 04 689 | 31 | 04 747 | 04 804 | 04 862 | 04 919 | 04 976 |
| 32 | 04 316 | 04 374 | 04 432 | 04 489 | 04 547 | 32 | 04 605 | 04 662 | 04 720 | 04 777 | 04 834 |
| 33 | 04 174 | 04 232 | 04 290 | 04 347 | 04 405 | 33 | 04 463 | 04 520 | 04 578 | 04 635 | 04 692 |
| 34 | 04 033 | 04 091 | 04 149 | 04 206 | 04 264 | 34 | 04 322 | 04 379 | 04 437 | 04 494 | 04 551 |
| 35 | 03 892 | 03 950 | 04 008 | 04 065 | 04 123 | 35 | 04 181 | 04 238 | 04 296 | 04 353 | 04 410 |
| 36 | 03 752 | 03 810 | 03 868 | 03 925 | 03 983 | 36 | 04 041 | 04 098 | 04 156 | 04 213 | 04 270 |

NITROGEN REDUCTION TABLE—*Continued*

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=760$ | 761 | 762 | 763 | 764 | t° | $p=765$ | 766 | 767 | 768 | 769 |
|-----------|---------|--------|--------|--------|--------|-----------|---------|--------|--------|--------|--------|
| 10 | 08 144 | 08 201 | 08 258 | 08 315 | 08 372 | 10 | 08 429 | 08 486 | 08 543 | 08 599 | 08 656 |
| 11 | 07 990 | 08 047 | 08 104 | 08 161 | 08 218 | 11 | 08 275 | 08 332 | 08 389 | 08 445 | 08 502 |
| 12 | 07 837 | 07 894 | 07 951 | 08 008 | 08 065 | 12 | 08 122 | 08 179 | 08 236 | 08 292 | 08 349 |
| 13 | 07 685 | 07 742 | 07 799 | 07 856 | 07 913 | 13 | 07 970 | 08 027 | 08 084 | 08 140 | 08 197 |
| 14 | 07 533 | 07 590 | 07 647 | 07 704 | 07 761 | 14 | 07 818 | 07 875 | 07 932 | 07 988 | 08 045 |
| 15 | 07 382 | 07 439 | 07 496 | 07 553 | 07 610 | 15 | 07 667 | 07 724 | 07 781 | 07 837 | 07 894 |
| 16 | 07 231 | 07 288 | 07 345 | 07 402 | 07 459 | 16 | 07 516 | 07 573 | 07 630 | 07 686 | 07 743 |
| 17 | 07 081 | 07 138 | 07 195 | 07 252 | 07 309 | 17 | 07 366 | 07 423 | 07 480 | 07 536 | 07 593 |
| 18 | 06 931 | 06 988 | 07 045 | 07 102 | 07 159 | 18 | 07 216 | 07 273 | 07 330 | 07 386 | 07 443 |
| 19 | 06 782 | 06 839 | 06 896 | 06 953 | 07 010 | 19 | 07 067 | 07 124 | 07 181 | 07 237 | 07 294 |
| 20 | 06 633 | 06 690 | 06 747 | 06 804 | 06 861 | 20 | 06 918 | 06 975 | 07 032 | 07 088 | 07 145 |
| 21 | 06 485 | 06 542 | 06 599 | 06 656 | 06 713 | 21 | 06 770 | 06 827 | 06 884 | 06 940 | 06 997 |
| 22 | 06 337 | 06 394 | 06 451 | 06 508 | 06 565 | 22 | 06 622 | 06 679 | 06 736 | 06 792 | 06 849 |
| 23 | 06 190 | 06 247 | 06 304 | 06 361 | 06 418 | 23 | 06 475 | 06 532 | 06 589 | 06 645 | 06 702 |
| 24 | 06 043 | 06 100 | 06 157 | 06 214 | 06 271 | 24 | 06 328 | 06 385 | 06 442 | 06 498 | 06 555 |
| 25 | 05 897 | 05 954 | 06 011 | 06 068 | 06 125 | 25 | 06 182 | 06 239 | 06 296 | 06 352 | 06 409 |
| 26 | 05 752 | 05 809 | 05 866 | 05 923 | 05 980 | 26 | 06 037 | 06 094 | 06 151 | 06 207 | 06 264 |
| 27 | 05 607 | 05 664 | 05 721 | 05 778 | 05 835 | 27 | 05 892 | 05 949 | 06 006 | 06 062 | 06 119 |
| 28 | 05 463 | 05 520 | 05 577 | 05 634 | 05 691 | 28 | 05 748 | 05 805 | 05 862 | 05 918 | 05 975 |
| 29 | 05 319 | 05 376 | 05 433 | 05 490 | 05 547 | 29 | 05 604 | 05 661 | 05 718 | 05 774 | 05 831 |
| 30 | 05 176 | 05 233 | 05 290 | 05 347 | 05 404 | 30 | 05 461 | 05 518 | 05 575 | 05 631 | 05 688 |
| 31 | 05 033 | 05 090 | 05 147 | 05 204 | 05 261 | 31 | 05 318 | 05 375 | 05 432 | 05 488 | 05 545 |
| 32 | 04 891 | 04 948 | 05 005 | 05 062 | 05 119 | 32 | 05 176 | 05 233 | 05 290 | 05 346 | 05 403 |
| 33 | 04 749 | 04 806 | 04 863 | 04 920 | 04 977 | 33 | 05 034 | 05 091 | 05 148 | 05 204 | 05 261 |
| 34 | 04 608 | 04 665 | 04 722 | 04 779 | 04 836 | 34 | 04 893 | 04 950 | 05 007 | 05 063 | 05 120 |
| 35 | 04 467 | 04 524 | 04 581 | 04 638 | 04 695 | 35 | 04 752 | 04 809 | 04 866 | 04 922 | 04 979 |
| 36 | 04 327 | 04 384 | 04 441 | 04 498 | 04 555 | 36 | 04 612 | 04 669 | 04 726 | 04 782 | 04 839 |

NITROGEN REDUCTION TABLE—*Continued*

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=770$ | 771 | 772 | 773 | 774 | t° | $p=775$ | 776 | 777 | 778 | 779 |
|-----------|---------|--------|--------|--------|--------|-----------|---------|--------|--------|--------|--------|
| 10 | 08 712 | 08 768 | 08 825 | 08 881 | 08 937 | 10 | 08 993 | 09 049 | 09 105 | 09 161 | 09 217 |
| 11 | 08 558 | 08 614 | 08 671 | 08 727 | 08 783 | 11 | 08 839 | 08 895 | 08 951 | 09 007 | 09 063 |
| 12 | 08 405 | 08 461 | 08 518 | 08 574 | 08 630 | 12 | 08 686 | 08 742 | 08 798 | 08 854 | 08 910 |
| 13 | 08 253 | 08 309 | 08 366 | 08 422 | 08 478 | 13 | 08 534 | 08 590 | 08 646 | 08 702 | 08 758 |
| 14 | 08 101 | 08 157 | 08 214 | 08 270 | 08 326 | 14 | 08 382 | 08 438 | 08 494 | 08 550 | 08 606 |
| 15 | 07 949 | 08 005 | 08 062 | 08 118 | 08 174 | 15 | 08 230 | 08 286 | 08 342 | 08 398 | 08 454 |
| 16 | 07 798 | 07 854 | 07 911 | 07 967 | 08 023 | 16 | 08 079 | 08 135 | 08 191 | 08 247 | 08 303 |
| 17 | 07 648 | 07 704 | 07 761 | 07 817 | 07 873 | 17 | 07 929 | 07 985 | 08 041 | 08 097 | 08 153 |
| 18 | 07 498 | 07 554 | 07 611 | 07 667 | 07 723 | 18 | 07 779 | 07 835 | 07 891 | 07 947 | 08 003 |
| 19 | 07 349 | 07 405 | 07 462 | 07 518 | 07 574 | 19 | 07 630 | 07 686 | 07 742 | 07 798 | 07 854 |
| 20 | 07 200 | 07 256 | 07 313 | 07 369 | 07 425 | 20 | 07 481 | 07 537 | 07 593 | 07 649 | 07 705 |
| 21 | 07 052 | 07 108 | 07 165 | 07 221 | 07 277 | 21 | 07 333 | 07 389 | 07 445 | 07 501 | 07 557 |
| 22 | 06 904 | 06 960 | 07 017 | 07 073 | 07 129 | 22 | 07 185 | 07 241 | 07 297 | 07 353 | 07 409 |
| 23 | 06 757 | 06 813 | 06 870 | 06 926 | 06 982 | 23 | 07 038 | 07 094 | 07 150 | 07 206 | 07 262 |
| 24 | 06 611 | 06 667 | 06 724 | 06 780 | 06 836 | 24 | 06 892 | 06 948 | 07 004 | 07 060 | 07 116 |
| 25 | 06 464 | 06 523 | 06 578 | 06 634 | 06 690 | 25 | 06 746 | 06 802 | 06 858 | 06 914 | 06 970 |
| 26 | 06 320 | 06 378 | 06 433 | 06 489 | 06 545 | 26 | 06 601 | 06 657 | 06 713 | 06 769 | 06 825 |
| 27 | 06 175 | 06 233 | 06 288 | 06 344 | 06 400 | 27 | 06 456 | 06 512 | 06 568 | 06 624 | 06 680 |
| 28 | 06 031 | 06 089 | 06 144 | 06 200 | 06 256 | 28 | 06 312 | 06 368 | 06 424 | 06 480 | 06 536 |
| 29 | 05 887 | 05 945 | 06 000 | 06 056 | 06 112 | 29 | 06 168 | 06 224 | 06 280 | 06 336 | 06 392 |
| 30 | 05 744 | 05 802 | 05 857 | 05 913 | 05 969 | 30 | 06 025 | 06 081 | 06 137 | 06 193 | 06 249 |
| 31 | 05 601 | 05 659 | 05 714 | 05 770 | 05 826 | 31 | 05 882 | 05 938 | 05 994 | 06 050 | 06 106 |
| 32 | 05 459 | 05 517 | 05 573 | 05 628 | 05 684 | 32 | 05 740 | 05 796 | 05 852 | 05 908 | 05 964 |
| 33 | 05 317 | 05 375 | 05 431 | 05 486 | 05 542 | 33 | 05 598 | 05 654 | 05 710 | 05 766 | 05 822 |
| 34 | 05 176 | 05 234 | 05 290 | 05 345 | 05 401 | 34 | 05 457 | 05 513 | 05 569 | 05 615 | 05 681 |
| 35 | 05 035 | 05 093 | 05 149 | 05 204 | 05 260 | 35 | 05 316 | 05 372 | 05 428 | 05 474 | 05 540 |
| 36 | 04 895 | 04 953 | 05 009 | 05 064 | 05 120 | 36 | 05 176 | 05 232 | 05 288 | 05 334 | 05 400 |

NITROGEN REDUCTION TABLE—*Continued*

One milliliter of nitrogen at 0° and 760 mm. pressure weighs 1.2505 mg. This table gives the logarithm of the weight of 1 ml. of nitrogen at t° and p mm.

| t° | $p=780$ | 781 | 782 | 783 | 784 | t° | $p=785$ | 786 | 787 | 788 | 789 |
|-----------|---------|--------|--------|--------|--------|-----------|---------|--------|--------|--------|--------|
| 10 | 09 272 | 09 328 | 09 384 | 09 439 | 09 495 | 10 | 09 550 | 09 605 | 09 660 | 09 716 | 09 771 |
| 11 | 09 118 | 09 174 | 09 230 | 09 285 | 09 341 | 11 | 09 396 | 09 451 | 09 506 | 09 562 | 09 617 |
| 12 | 08 965 | 09 021 | 09 077 | 09 132 | 09 188 | 12 | 09 243 | 09 298 | 09 353 | 09 409 | 09 464 |
| 13 | 08 813 | 08 869 | 08 925 | 08 980 | 09 036 | 13 | 09 091 | 09 146 | 09 201 | 09 257 | 09 312 |
| 14 | 08 661 | 08 717 | 08 773 | 08 828 | 08 884 | 14 | 08 939 | 08 994 | 09 049 | 09 105 | 09 162 |
| 15 | 08 509 | 08 565 | 08 621 | 08 676 | 08 732 | 15 | 08 787 | 08 842 | 08 897 | 08 953 | 09 008 |
| 16 | 08 358 | 08 414 | 08 470 | 08 525 | 08 581 | 16 | 08 636 | 08 691 | 08 746 | 08 802 | 08 857 |
| 17 | 08 208 | 08 264 | 08 320 | 08 375 | 08 431 | 17 | 08 486 | 08 541 | 08 596 | 08 652 | 08 707 |
| 18 | 08 058 | 08 114 | 08 170 | 08 225 | 08 281 | 18 | 08 336 | 08 391 | 08 446 | 08 502 | 08 557 |
| 19 | 07 909 | 07 965 | 08 021 | 08 076 | 08 132 | 19 | 08 187 | 08 242 | 08 297 | 08 353 | 08 408 |
| 20 | 07 760 | 07 816 | 07 872 | 07 927 | 07 983 | 20 | 08 038 | 08 093 | 08 148 | 08 204 | 08 259 |
| 21 | 07 612 | 07 668 | 07 724 | 07 779 | 07 835 | 21 | 07 890 | 07 945 | 08 000 | 08 056 | 08 111 |
| 22 | 07 464 | 07 520 | 07 576 | 07 631 | 07 687 | 22 | 07 742 | 07 797 | 07 852 | 07 908 | 07 963 |
| 23 | 07 317 | 07 373 | 07 429 | 07 484 | 07 540 | 23 | 07 595 | 07 650 | 07 705 | 07 761 | 07 816 |
| 24 | 07 171 | 07 227 | 07 283 | 07 338 | 07 394 | 24 | 07 449 | 07 504 | 07 559 | 07 615 | 07 670 |
| 25 | 07 025 | 07 081 | 07 137 | 07 192 | 07 248 | 25 | 07 303 | 07 358 | 07 413 | 07 469 | 07 524 |
| 26 | 06 880 | 06 936 | 06 992 | 07 047 | 07 103 | 26 | 07 158 | 07 213 | 07 268 | 07 324 | 07 379 |
| 27 | 06 735 | 06 791 | 06 847 | 06 902 | 06 958 | 27 | 07 013 | 07 068 | 07 123 | 07 179 | 07 234 |
| 28 | 06 591 | 06 627 | 06 703 | 06 758 | 06 814 | 28 | 06 869 | 06 924 | 06 979 | 07 035 | 07 090 |
| 29 | 06 447 | 06 483 | 06 559 | 06 614 | 06 670 | 29 | 06 725 | 06 780 | 06 835 | 06 891 | 06 946 |
| 30 | 06 304 | 06 340 | 06 416 | 06 471 | 06 527 | 30 | 06 582 | 06 637 | 06 692 | 06 748 | 06 803 |
| 31 | 06 161 | 06 197 | 06 273 | 06 328 | 06 387 | 31 | 06 439 | 06 494 | 06 549 | 06 605 | 06 660 |
| 32 | 06 019 | 06 055 | 06 131 | 06 186 | 06 245 | 32 | 06 297 | 06 352 | 06 407 | 06 463 | 06 518 |
| 33 | 05 877 | 05 913 | 05 989 | 06 044 | 06 103 | 33 | 06 155 | 06 210 | 06 265 | 06 321 | 06 376 |
| 34 | 05 736 | 05 772 | 05 848 | 05 903 | 05 962 | 34 | 06 014 | 06 069 | 06 124 | 06 180 | 06 235 |
| 35 | 05 595 | 05 631 | 05 707 | 05 762 | 05 821 | 35 | 05 873 | 05 928 | 05 983 | 06 039 | 06 094 |
| 36 | 05 455 | 05 491 | 05 567 | 05 622 | 05 681 | 36 | 05 733 | 05 788 | 05 843 | 05 899 | 05 954 |

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts | | | |
|-----|--------|------|------|------|------|------|------|------|------|------|-------------|------|------|------|
| 100 | 00 000 | 043 | 087 | 130 | 173 | 217 | 260 | 303 | 346 | 389 | | | | |
| 01 | 432 | 475 | 518 | 561 | 604 | 647 | 689 | 732 | 775 | 817 | | | | |
| 02 | 00 860 | 903 | 945 | 988 | *030 | *072 | *115 | *157 | *199 | *242 | 1 | 44 | 43 | 42 |
| 03 | 01 284 | 326 | 368 | 410 | 452 | 494 | 536 | 578 | 620 | 662 | 2 | 8.8 | 8.6 | 8.4 |
| 04 | 01 703 | 745 | 787 | 828 | 870 | 912 | 955 | 995 | *036 | *078 | 3 | 13.2 | 12.9 | 12.6 |
| 05 | 02 119 | 160 | 202 | 243 | 284 | 325 | 366 | 407 | 449 | 490 | 4 | 17.6 | 17.2 | 16.8 |
| 06 | 531 | 572 | 612 | 653 | 694 | 735 | 776 | 816 | 857 | 898 | 5 | 22.0 | 21.5 | 21.0 |
| 07 | 02 938 | 979 | *019 | *060 | *100 | *141 | *181 | *222 | *262 | *302 | 6 | 26.4 | 25.8 | 25.2 |
| 08 | 03 342 | 383 | 423 | 463 | 503 | 543 | 583 | 623 | 663 | 703 | 7 | 30.8 | 30.1 | 29.4 |
| 09 | 03 743 | 782 | 822 | 862 | 902 | 941 | 981 | *021 | *060 | *100 | 8 | 35.2 | 34.4 | 33.6 |
| 110 | 04 139 | 179 | 218 | 258 | 297 | 336 | 376 | 415 | 454 | 493 | 9 | 39.6 | 38.7 | 37.8 |
| 11 | 532 | 571 | 610 | 650 | 689 | 727 | 766 | 805 | 844 | 883 | | | | |
| 12 | 04 922 | 961 | 999 | *038 | *077 | *115 | *154 | *192 | *231 | *269 | 1 | 41 | 40 | 39 |
| 13 | 05 308 | 346 | 385 | 423 | 461 | 500 | 538 | 576 | 614 | 652 | 2 | 4.1 | 4 | 3.9 |
| 14 | 05 690 | 729 | 767 | 805 | 843 | 881 | 918 | 956 | 994 | *032 | 3 | 8.2 | 8 | 7.8 |
| 15 | 06 070 | 108 | 145 | 183 | 221 | 258 | 296 | 333 | 371 | 408 | 4 | 12.3 | 12 | 11.7 |
| 16 | 446 | 483 | 521 | 558 | 595 | 633 | 670 | 707 | 744 | 781 | 5 | 16.3 | 16 | 15.6 |
| 17 | 06 819 | 856 | 893 | 930 | 967 | *004 | *041 | *078 | *115 | *151 | 6 | 20.5 | 20 | 19.6 |
| 18 | 07 188 | 225 | 262 | 298 | 335 | 372 | 408 | 445 | 482 | 518 | 7 | 24.6 | 24 | 23.4 |
| 19 | 555 | 591 | 628 | 664 | 700 | 737 | 773 | 809 | 846 | 882 | 8 | 28.7 | 28 | 27.3 |
| 120 | 07 918 | 954 | 990 | *027 | *063 | *099 | *135 | *171 | *207 | *243 | 9 | 32.8 | 32 | 31.2 |
| 21 | 08 279 | 314 | 350 | 386 | 422 | 458 | 493 | 529 | 565 | 600 | | | | |
| 22 | 636 | 672 | 707 | 743 | 778 | 814 | 849 | 884 | 920 | 955 | 1 | 38 | 37 | 36 |
| 23 | 08 991 | *026 | *061 | *096 | *132 | *167 | *202 | *237 | *272 | *307 | 2 | 3.8 | 3.7 | 3.6 |
| 24 | 09 342 | 377 | 412 | 447 | 482 | 517 | 552 | 587 | 621 | 656 | 3 | 7.6 | 7.4 | 7.2 |
| 25 | 09 691 | 726 | 760 | 795 | 830 | 864 | 899 | 934 | 968 | *003 | 4 | 11.4 | 11.1 | 10.8 |
| 26 | 10 037 | 072 | 106 | 140 | 175 | 209 | 243 | 278 | 312 | 346 | 5 | 15.2 | 14.8 | 14.4 |
| 27 | 380 | 415 | 449 | 483 | 517 | 551 | 585 | 619 | 653 | 687 | 6 | 19.0 | 18.5 | 18.0 |
| 28 | 10 721 | 755 | 789 | 823 | 857 | 890 | 924 | 958 | 992 | *025 | 7 | 22.8 | 22.2 | 21.6 |
| 29 | 11 059 | 093 | 126 | 160 | 193 | 227 | 261 | 294 | 327 | 361 | 8 | 26.6 | 25.9 | 25.2 |
| 130 | 394 | 428 | 461 | 494 | 528 | 561 | 594 | 628 | 661 | 694 | 9 | 30.4 | 29.6 | 28.8 |
| 31 | 11 727 | 760 | 793 | 826 | 860 | 893 | 926 | 959 | 992 | *024 | | | | |
| 32 | 12 057 | 090 | 123 | 156 | 189 | 222 | 256 | 287 | 320 | 352 | 1 | 35 | 34 | 33 |
| 33 | 385 | 418 | 450 | 483 | 516 | 548 | 581 | 613 | 646 | 678 | 2 | 3.5 | 3.4 | 3.3 |
| 34 | 12 710 | 743 | 775 | 808 | 840 | 872 | 905 | 937 | 969 | *001 | 3 | 7.5 | 7.0 | 6.8 |
| 35 | 13 033 | 066 | 098 | 130 | 162 | 194 | 226 | 258 | 290 | 322 | 4 | 10.5 | 10.2 | 9.9 |
| 36 | 354 | 386 | 418 | 450 | 481 | 513 | 545 | 577 | 609 | 640 | 5 | 14.0 | 13.6 | 13.2 |
| 37 | 672 | 704 | 735 | 767 | 799 | 830 | 862 | 893 | 925 | 956 | 6 | 17.5 | 17.0 | 16.5 |
| 38 | 13 988 | *019 | *051 | *082 | *114 | *145 | *176 | *208 | *239 | *270 | 7 | 21.5 | 20.4 | 19.8 |
| 39 | 14 301 | 333 | 364 | 395 | 426 | 457 | 489 | 520 | 551 | 582 | 8 | 24.5 | 23.8 | 23.1 |
| 140 | 613 | 644 | 675 | 706 | 737 | 768 | 799 | 829 | 860 | 891 | 9 | 28.0 | 27.2 | 26.4 |
| 41 | 14 922 | 953 | 983 | *014 | *045 | *076 | *106 | *137 | *168 | *198 | | | | |
| 42 | 15 229 | 259 | 290 | 320 | 351 | 381 | 412 | 442 | 473 | 503 | 1 | 32 | 31 | 30 |
| 43 | 534 | 564 | 594 | 625 | 655 | 685 | 715 | 746 | 776 | 806 | 2 | 3.2 | 3.1 | 3 |
| 44 | 15 836 | 866 | 897 | 927 | 957 | 987 | *017 | *047 | *077 | *107 | 3 | 6.4 | 6.2 | 6 |
| 45 | 16 137 | 167 | 197 | 227 | 256 | 286 | 316 | 346 | 376 | 406 | 4 | 9.6 | 9.3 | 9 |
| 46 | 435 | 465 | 495 | 524 | 554 | 584 | 613 | 643 | 673 | 702 | 5 | 12.8 | 12.4 | 12 |
| 47 | 16 732 | 761 | 791 | 820 | 850 | 879 | 909 | 938 | 967 | 997 | 6 | 16.0 | 15.5 | 15 |
| 48 | 17 026 | 056 | 085 | 114 | 143 | 173 | 202 | 231 | 260 | 289 | 7 | 19.2 | 18.6 | 18 |
| 49 | 319 | 348 | 377 | 406 | 435 | 464 | 493 | 522 | 551 | 580 | 8 | 22.4 | 21.8 | 21 |
| 150 | 17 609 | 638 | 667 | 696 | 725 | 754 | 782 | 811 | 840 | 869 | 9 | 25.2 | 24.7 | 24 |
| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts | | | |

| Prop. Parts | | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------|--|--|-----|--------|--------|-----|------|------|------|------|------|------|------|
| | | | 150 | 17 609 | 638 | 667 | 696 | 725 | 754 | 782 | 811 | 840 | 869 |
| | | | | 51 | 17 898 | 926 | 955 | 984 | *013 | *041 | *070 | *099 | *127 |
| | | | | 52 | 18 184 | 213 | 241 | 270 | 298 | 327 | 355 | 384 | 412 |
| | | | | 53 | 469 | 498 | 526 | 554 | 583 | 611 | 639 | 667 | 696 |
| | | | | 54 | 18 752 | 780 | 808 | 837 | 865 | 893 | 921 | 949 | 977 |
| | | | | 55 | 19 033 | 061 | 089 | 117 | 145 | 173 | 201 | 229 | 257 |
| | | | | 56 | 312 | 340 | 368 | 396 | 424 | 451 | 479 | 507 | 535 |
| | | | | 57 | 590 | 618 | 645 | 673 | 700 | 728 | 756 | 783 | 811 |
| | | | | 58 | 19 866 | 893 | 921 | 948 | 976 | *003 | *030 | *058 | *085 |
| | | | | 59 | 20 140 | 167 | 194 | 222 | 249 | 276 | 303 | 330 | 358 |
| | | | | 60 | 20 414 | 241 | 268 | 295 | 322 | 349 | 376 | 403 | 430 |
| | | | | 61 | 683 | 710 | 737 | 763 | 790 | 817 | 844 | 871 | 898 |
| | | | | 62 | 20 952 | 978 | *005 | *032 | *059 | *085 | *112 | *139 | *165 |
| | | | | 63 | 21 219 | 245 | 272 | 299 | 325 | 352 | 378 | 405 | 431 |
| | | | | 64 | 484 | 511 | 537 | 564 | 590 | 617 | 643 | 669 | 696 |
| | | | | 65 | 21 748 | 775 | 801 | 827 | 854 | 880 | 906 | 932 | 958 |
| | | | | 66 | 22 011 | 037 | 063 | 089 | 115 | 141 | 167 | 194 | 220 |
| | | | | 67 | 272 | 298 | 324 | 350 | 376 | 401 | 427 | 453 | 479 |
| | | | | 68 | 531 | 557 | 583 | 608 | 634 | 660 | 686 | 712 | 737 |
| | | | | 69 | 22 789 | 814 | 840 | 866 | 891 | 917 | 943 | 968 | *019 |
| | | | | 70 | 23 045 | 070 | 096 | 121 | 147 | 172 | 198 | 223 | 249 |
| | | | | 71 | 300 | 325 | 350 | 376 | 401 | 426 | 452 | 477 | 502 |
| | | | | 72 | 553 | 578 | 603 | 629 | 654 | 679 | 704 | 729 | 754 |
| | | | | 73 | 23 805 | 830 | 855 | 880 | 905 | 930 | 955 | 980 | *005 |
| | | | | 74 | 24 055 | 080 | 105 | 130 | 155 | 180 | 204 | 229 | 254 |
| | | | | 75 | 304 | 329 | 353 | 378 | 403 | 428 | 452 | 477 | 502 |
| | | | | 76 | 551 | 576 | 601 | 625 | 650 | 674 | 699 | 724 | 748 |
| | | | | 77 | 24 797 | 822 | 846 | 871 | 895 | 920 | 944 | 969 | 993 |
| | | | | 78 | 25 042 | 066 | 091 | 115 | 139 | 164 | 188 | 212 | 237 |
| | | | | 79 | 285 | 310 | 334 | 358 | 382 | 406 | 431 | 455 | 479 |
| | | | | 80 | 527 | 551 | 575 | 600 | 624 | 648 | 672 | 696 | 720 |
| | | | | 81 | 25 768 | 792 | 816 | 840 | 864 | 888 | 912 | 935 | 959 |
| | | | | 82 | 26 007 | 031 | 055 | 079 | 102 | 126 | 150 | 174 | 198 |
| | | | | 83 | 245 | 269 | 293 | 316 | 340 | 364 | 387 | 411 | 435 |
| | | | | 84 | 482 | 505 | 529 | 553 | 576 | 600 | 623 | 647 | 670 |
| | | | | 85 | 717 | 741 | 764 | 788 | 811 | 834 | 858 | 881 | 905 |
| | | | | 86 | 26 951 | 975 | 998 | *021 | *045 | *068 | *091 | *114 | *138 |
| | | | | 87 | 27 184 | 207 | 231 | 254 | 277 | 300 | 323 | 346 | 370 |
| | | | | 88 | 416 | 439 | 462 | 485 | 508 | 531 | 554 | 577 | 600 |
| | | | | 89 | 646 | 669 | 692 | 715 | 738 | 761 | 784 | 807 | 830 |
| | | | | 90 | 885 | 907 | 929 | 951 | 973 | 994 | *016 | *038 | *060 |
| | | | | 91 | 28 103 | 126 | 149 | 171 | 194 | 217 | 240 | 262 | 285 |
| | | | | 92 | 330 | 353 | 375 | 398 | 421 | 443 | 466 | 488 | 511 |
| | | | | 93 | 556 | 578 | 601 | 623 | 646 | 668 | 691 | 713 | 735 |
| | | | | 94 | 28 780 | 803 | 825 | 847 | 870 | 892 | 914 | 937 | 959 |
| | | | | 95 | 29 003 | 026 | 048 | 070 | 092 | 115 | 137 | 159 | 181 |
| | | | | 96 | 226 | 248 | 270 | 292 | 314 | 336 | 358 | 380 | 403 |
| | | | | 97 | 447 | 469 | 491 | 513 | 535 | 557 | 579 | 601 | 623 |
| | | | | 98 | 667 | 688 | 710 | 732 | 754 | 776 | 798 | 820 | 842 |
| | | | | 99 | 29 885 | 907 | 929 | 951 | 973 | 994 | *016 | *038 | *060 |
| | | | | 100 | 30 103 | 125 | 146 | 168 | 190 | 211 | 233 | 255 | 276 |
| Prop. Parts | | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |
|-----|--------|------|------|------|------|------|------|------|------|------|-------------|
| 200 | 30 103 | 125 | 146 | 168 | 190 | 211 | 233 | 255 | 276 | 298 | |
| 01 | 320 | 341 | 363 | 384 | 406 | 428 | 449 | 471 | 492 | 514 | |
| 02 | 535 | 557 | 578 | 600 | 621 | 643 | 664 | 685 | 707 | 728 | |
| 03 | 750 | 771 | 792 | 814 | 835 | 856 | 878 | 899 | 920 | 942 | |
| 04 | 30 963 | 984 | *006 | *027 | *048 | *069 | *091 | *112 | *133 | *154 | |
| 05 | 31 175 | 197 | 218 | 239 | 260 | 281 | 302 | 323 | 345 | 366 | |
| 06 | 387 | 408 | 429 | 450 | 471 | 492 | 513 | 534 | 555 | 576 | |
| 07 | 597 | 618 | 639 | 660 | 681 | 702 | 723 | 744 | 765 | 785 | |
| 08 | 31 806 | 827 | 848 | 869 | 890 | 911 | 931 | 952 | 973 | 994 | |
| 09 | 32 015 | 035 | 056 | 077 | 098 | 118 | 139 | 160 | 181 | 201 | |
| 210 | 222 | 243 | 263 | 284 | 305 | 325 | 346 | 366 | 387 | 408 | |
| 11 | 428 | 449 | 469 | 490 | 510 | 531 | 552 | 572 | 593 | 613 | |
| 12 | 634 | 654 | 675 | 695 | 715 | 736 | 756 | 777 | 797 | 818 | |
| 13 | 32 838 | 858 | 879 | 899 | 919 | 940 | 960 | 980 | *001 | *021 | |
| 14 | 33 041 | 062 | 082 | 102 | 122 | 143 | 163 | 183 | 203 | 224 | |
| 15 | 244 | 264 | 284 | 304 | 325 | 345 | 365 | 385 | 405 | 425 | |
| 16 | 445 | 465 | 486 | 506 | 526 | 546 | 566 | 586 | 606 | 626 | |
| 17 | 646 | 666 | 686 | 706 | 726 | 746 | 766 | 786 | 806 | 826 | |
| 18 | 33 846 | 866 | 885 | 905 | 925 | 945 | 965 | 985 | *005 | *025 | |
| 19 | 34 044 | 064 | 084 | 104 | 124 | 143 | 163 | 183 | 203 | 223 | |
| 220 | 242 | 262 | 282 | 301 | 321 | 341 | 361 | 380 | 400 | 420 | |
| 21 | 439 | 459 | 479 | 498 | 518 | 537 | 557 | 577 | 596 | 616 | |
| 22 | 635 | 655 | 674 | 694 | 713 | 733 | 753 | 772 | 792 | 811 | |
| 23 | 34 830 | 850 | 869 | 889 | 908 | 928 | 947 | 967 | 986 | *005 | |
| 24 | 35 025 | 044 | 064 | 083 | 102 | 122 | 141 | 160 | 180 | 199 | |
| 25 | 218 | 238 | 257 | 276 | 295 | 315 | 334 | 353 | 372 | 392 | |
| 26 | 411 | 430 | 449 | 468 | 488 | 507 | 526 | 545 | 564 | 583 | |
| 27 | 603 | 622 | 641 | 660 | 679 | 698 | 717 | 736 | 755 | 774 | |
| 28 | 793 | 813 | 832 | 851 | 870 | 889 | 908 | 927 | 946 | 965 | |
| 29 | 35 984 | *003 | *021 | *040 | *059 | *078 | *097 | *116 | *135 | *154 | |
| 230 | 36 173 | 192 | 211 | 229 | 248 | 267 | 286 | 305 | 324 | 342 | |
| 31 | 361 | 380 | 399 | 418 | 436 | 455 | 474 | 493 | 511 | 530 | |
| 32 | 549 | 568 | 586 | 605 | 624 | 642 | 661 | 680 | 698 | 717 | |
| 33 | 736 | 754 | 773 | 791 | 810 | 829 | 847 | 866 | 884 | 903 | |
| 34 | 36 922 | 940 | 959 | 977 | 996 | *014 | *033 | *051 | *070 | *088 | |
| 35 | 37 107 | 125 | 144 | 162 | 181 | 199 | 218 | 236 | 254 | 273 | |
| 36 | 291 | 310 | 328 | 346 | 365 | 383 | 401 | 420 | 438 | 457 | |
| 37 | 475 | 493 | 511 | 530 | 548 | 566 | 585 | 603 | 621 | 639 | |
| 38 | 668 | 676 | 694 | 712 | 731 | 749 | 767 | 785 | 803 | 822 | |
| 39 | 37 840 | 858 | 876 | 894 | 912 | 931 | 949 | 967 | 985 | *003 | |
| 240 | 38 021 | 039 | 057 | 075 | 093 | 112 | 130 | 148 | 166 | 184 | |
| 41 | 202 | 220 | 238 | 256 | 274 | 292 | 310 | 328 | 346 | 364 | |
| 42 | 382 | 399 | 417 | 435 | 453 | 471 | 489 | 507 | 525 | 543 | |
| 43 | 561 | 578 | 596 | 614 | 632 | 650 | 668 | 686 | 703 | 721 | |
| 44 | 739 | 757 | 775 | 792 | 810 | 828 | 846 | 863 | 881 | 899 | |
| 45 | 38 917 | 934 | 952 | 970 | 987 | *005 | *023 | *041 | *058 | *076 | |
| 46 | 39 094 | 111 | 129 | 146 | 164 | 182 | 199 | 217 | 235 | 252 | |
| 47 | 270 | 287 | 305 | 322 | 340 | 358 | 375 | 393 | 410 | 428 | |
| 48 | 445 | 463 | 480 | 498 | 515 | 533 | 550 | 568 | 585 | 602 | |
| 49 | 620 | 637 | 655 | 672 | 690 | 707 | 724 | 742 | 759 | 777 | |
| 250 | 39 794 | 811 | 829 | 846 | 863 | 881 | 898 | 915 | 933 | 950 | |
| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |

22 21
1 2.2 2.1
2 4.4 4.2
3 6.6 6.3
4 8.8 8.4
5 11.0 10.5
6 13.2 12.6
7 15.4 14.7
8 17.6 16.8
9 19.8 18.9

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19
1 1.9
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5 9.5
6 11.4
7 13.3
8 15.2
9 17.1

18
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4 7.2
5 9.0
6 10.8
7 12.6
8 14.4
9 16.2

17
1 1.7
2 3.4
3 5.1
4 6.8
5 8.5
6 10.2
7 11.9
8 13.6
9 15.3

| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------|--|-----|--------|------|------|------|------|------|------|------|------|------|
| | | 250 | 39 794 | 811 | 829 | 846 | 863 | 881 | 898 | 915 | 933 | 950 |
| | | 51 | 39 967 | 985 | *002 | *019 | *037 | *054 | *071 | *088 | *106 | *123 |
| | | 52 | 40 140 | 157 | 175 | 192 | 209 | 226 | 243 | 261 | 278 | 295 |
| | | 53 | 312 | 329 | 346 | 364 | 381 | 398 | 415 | 432 | 449 | 466 |
| | | 54 | 483 | 500 | 518 | 535 | 552 | 569 | 586 | 603 | 620 | 637 |
| | | 55 | 654 | 671 | 688 | 705 | 722 | 739 | 756 | 773 | 790 | 807 |
| | | 56 | 824 | 841 | 858 | 875 | 892 | 909 | 926 | 943 | 960 | 976 |
| | | 57 | 40 993 | *010 | *027 | *044 | *061 | *078 | *095 | *111 | *128 | *145 |
| | | 58 | 41 162 | 179 | 196 | 212 | 229 | 246 | 263 | 280 | 296 | 313 |
| | | 59 | 330 | 347 | 363 | 380 | 397 | 414 | 430 | 447 | 464 | 481 |
| | | 260 | 497 | 514 | 531 | 547 | 564 | 581 | 597 | 614 | 631 | 647 |
| | | 61 | 664 | 681 | 697 | 714 | 731 | 747 | 764 | 780 | 797 | 814 |
| | | 62 | 830 | 847 | 863 | 880 | 896 | 913 | 929 | 946 | 963 | 979 |
| | | 63 | 41 996 | *012 | *029 | *045 | *062 | *078 | *095 | *111 | *127 | *144 |
| | | 64 | 42 160 | 177 | 193 | 210 | 226 | 243 | 259 | 275 | 292 | 308 |
| | | 65 | 325 | 341 | 357 | 374 | 390 | 406 | 423 | 439 | 455 | 472 |
| | | 66 | 488 | 504 | 521 | 537 | 553 | 570 | 586 | 602 | 619 | 635 |
| | | 67 | 651 | 667 | 684 | 700 | 716 | 732 | 749 | 765 | 781 | 797 |
| | | 68 | 813 | 830 | 846 | 862 | 878 | 894 | 911 | 927 | 943 | 959 |
| | | 69 | 42 975 | 991 | *008 | *024 | *040 | *056 | *072 | *088 | *104 | *120 |
| | | 270 | 43 136 | 152 | 169 | 185 | 201 | 217 | 233 | 249 | 265 | 281 |
| | | 71 | 297 | 313 | 329 | 345 | 361 | 377 | 393 | 409 | 425 | 441 |
| | | 72 | 457 | 473 | 489 | 505 | 521 | 537 | 553 | 569 | 584 | 600 |
| | | 73 | 616 | 632 | 648 | 664 | 680 | 696 | 712 | 727 | 743 | 759 |
| | | 74 | 775 | 791 | 807 | 823 | 838 | 854 | 870 | 886 | 902 | 917 |
| | | 75 | 43 933 | 949 | 965 | 981 | 996 | *012 | *028 | *044 | *059 | *075 |
| | | 76 | 44 091 | 107 | 122 | 138 | 154 | 170 | 185 | 201 | 217 | 232 |
| | | 77 | 248 | 264 | 279 | 295 | 311 | 326 | 342 | 358 | 373 | 389 |
| | | 78 | 404 | 420 | 436 | 451 | 467 | 483 | 498 | 514 | 529 | 545 |
| | | 79 | 560 | 576 | 592 | 607 | 623 | 638 | 654 | 669 | 685 | 700 |
| | | 280 | 716 | 731 | 747 | 762 | 778 | 793 | 809 | 824 | 840 | 855 |
| | | 81 | 44 871 | 886 | 902 | 917 | 932 | 948 | 963 | 979 | 994 | *010 |
| | | 82 | 45 025 | 040 | 056 | 071 | 086 | 102 | 117 | 133 | 148 | 163 |
| | | 83 | 179 | 194 | 209 | 225 | 240 | 255 | 271 | 286 | 301 | 317 |
| | | 84 | 332 | 347 | 362 | 378 | 393 | 408 | 423 | 439 | 454 | 469 |
| | | 85 | 484 | 500 | 515 | 530 | 545 | 561 | 576 | 591 | 606 | 621 |
| | | 86 | 637 | 652 | 667 | 682 | 697 | 712 | 728 | 743 | 758 | 773 |
| | | 87 | 788 | 803 | 818 | 834 | 849 | 864 | 879 | 894 | 909 | 924 |
| | | 88 | 45 939 | 954 | 969 | 984 | *000 | *015 | *030 | *045 | *060 | *075 |
| | | 89 | 46 090 | 105 | 120 | 135 | 150 | 165 | 180 | 195 | 210 | 225 |
| | | 290 | 240 | 255 | 270 | 285 | 300 | 315 | 330 | 345 | 359 | 374 |
| | | 91 | 389 | 404 | 419 | 434 | 449 | 464 | 479 | 494 | 509 | 523 |
| | | 92 | 538 | 553 | 568 | 583 | 598 | 613 | 627 | 642 | 657 | 672 |
| | | 93 | 687 | 702 | 716 | 731 | 746 | 761 | 776 | 790 | 805 | 820 |
| | | 94 | 835 | 850 | 864 | 879 | 894 | 909 | 923 | 938 | 953 | 967 |
| | | 95 | 46 982 | 997 | *012 | *026 | *041 | *056 | *070 | *085 | *100 | *114 |
| | | 96 | 47 129 | 144 | 159 | 173 | 188 | 202 | 217 | 232 | 246 | 261 |
| | | 97 | 276 | 290 | 305 | 319 | 334 | 349 | 363 | 378 | 392 | 407 |
| | | 98 | 422 | 436 | 451 | 465 | 480 | 494 | 509 | 524 | 538 | 553 |
| | | 99 | 567 | 582 | 596 | 611 | 625 | 640 | 654 | 669 | 683 | 698 |
| | | 300 | 47 712 | 727 | 741 | 756 | 770 | 784 | 799 | 813 | 828 | 842 |
| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |
|-----|--------|------|------|------|------|------|------|------|------|------|-------------|
| 300 | 47 712 | 727 | 741 | 756 | 770 | 784 | 799 | 813 | 828 | 842 | |
| 01 | 47 857 | 871 | 885 | 900 | 914 | 929 | 943 | 958 | 972 | 986 | |
| 02 | 48 001 | 015 | 029 | 044 | 058 | 073 | 087 | 101 | 116 | 130 | |
| 03 | 144 | 159 | 173 | 187 | 202 | 216 | 230 | 244 | 259 | 273 | |
| 04 | 287 | 302 | 316 | 330 | 344 | 359 | 373 | 387 | 401 | 416 | |
| 05 | 430 | 444 | 458 | 473 | 487 | 501 | 515 | 530 | 544 | 558 | |
| 06 | 572 | 586 | 601 | 615 | 629 | 643 | 657 | 671 | 686 | 700 | |
| 07 | 714 | 728 | 742 | 756 | 770 | 785 | 799 | 813 | 827 | 841 | |
| 08 | 855 | 869 | 883 | 897 | 911 | 926 | 940 | 954 | 968 | 982 | |
| 09 | 48 996 | *010 | *024 | *038 | *052 | *066 | *080 | *094 | *108 | *122 | |
| 310 | 49 136 | 150 | 164 | 178 | 192 | 206 | 220 | 234 | 248 | 262 | |
| 11 | 276 | 290 | 304 | 318 | 332 | 346 | 360 | 374 | 388 | 402 | |
| 12 | 415 | 429 | 443 | 457 | 471 | 485 | 499 | 513 | 527 | 541 | |
| 13 | 554 | 568 | 582 | 596 | 610 | 624 | 638 | 651 | 665 | 679 | |
| 14 | 693 | 707 | 721 | 734 | 748 | 762 | 776 | 790 | 803 | 817 | |
| 15 | 831 | 845 | 859 | 872 | 886 | 900 | 914 | 927 | 941 | 955 | |
| 16 | 49 969 | 982 | 996 | *010 | *024 | *037 | *051 | *065 | *079 | *092 | |
| 17 | 50 106 | 120 | 133 | 147 | 161 | 174 | 188 | 202 | 215 | 229 | |
| 18 | 243 | 256 | 270 | 284 | 297 | 311 | 325 | 338 | 352 | 365 | |
| 19 | 379 | 393 | 406 | 420 | 433 | 447 | 461 | 474 | 488 | 501 | |
| 320 | 515 | 529 | 542 | 556 | 569 | 583 | 596 | 610 | 623 | 637 | |
| 21 | 651 | 664 | 678 | 691 | 705 | 718 | 732 | 745 | 759 | 772 | |
| 22 | 786 | 799 | 813 | 826 | 840 | 853 | 866 | 880 | 893 | 907 | |
| 23 | 50 920 | 934 | 947 | 961 | 974 | 987 | *001 | *014 | *028 | *041 | |
| 24 | 51 055 | 068 | 081 | 095 | 108 | 121 | 135 | 148 | 162 | 175 | |
| 25 | 188 | 202 | 215 | 228 | 242 | 255 | 268 | 282 | 295 | 308 | |
| 26 | 322 | 335 | 348 | 362 | 375 | 388 | 402 | 415 | 428 | 441 | |
| 27 | 455 | 468 | 481 | 495 | 508 | 521 | 534 | 548 | 561 | 574 | |
| 28 | 587 | 601 | 614 | 627 | 640 | 654 | 667 | 680 | 693 | 706 | |
| 29 | 720 | 733 | 746 | 759 | 772 | 786 | 799 | 812 | 825 | 838 | |
| 330 | 851 | 865 | 878 | 891 | 904 | 917 | 930 | 943 | 957 | 970 | |
| 31 | 51 983 | 996 | *009 | *022 | *035 | *048 | *061 | *075 | *088 | *101 | |
| 32 | 52 114 | 127 | 140 | 153 | 166 | 179 | 192 | 205 | 218 | 231 | |
| 33 | 244 | 257 | 270 | 284 | 297 | 310 | 323 | 336 | 349 | 362 | |
| 34 | 375 | 388 | 401 | 414 | 427 | 440 | 453 | 466 | 479 | 492 | |
| 35 | 504 | 517 | 530 | 543 | 556 | 569 | 582 | 595 | 608 | 621 | |
| 36 | 634 | 647 | 660 | 673 | 686 | 699 | 711 | 724 | 737 | 750 | |
| 37 | 763 | 776 | 789 | 802 | 815 | 827 | 840 | 853 | 866 | 879 | |
| 38 | 52 892 | 905 | 917 | 930 | 943 | 956 | 969 | 982 | 994 | *007 | |
| 39 | 53 020 | 033 | 046 | 058 | 071 | 084 | 097 | 110 | 122 | 135 | |
| 340 | 148 | 161 | 173 | 186 | 199 | 212 | 224 | 237 | 250 | 263 | |
| 41 | 275 | 288 | 301 | 314 | 326 | 339 | 352 | 364 | 377 | 390 | |
| 42 | 403 | 415 | 428 | 441 | 453 | 466 | 479 | 491 | 504 | 517 | |
| 43 | 529 | 542 | 555 | 567 | 580 | 593 | 605 | 618 | 631 | 643 | |
| 44 | 656 | 668 | 681 | 694 | 706 | 719 | 732 | 744 | 757 | 769 | |
| 45 | 782 | 794 | 807 | 820 | 832 | 845 | 857 | 870 | 882 | 895 | |
| 46 | 53 908 | 920 | 933 | 945 | 958 | 970 | 983 | 995 | *008 | *020 | |
| 47 | 54 033 | 045 | 058 | 070 | 083 | 095 | 108 | 120 | 133 | 145 | |
| 48 | 158 | 170 | 183 | 195 | 208 | 220 | 233 | 245 | 258 | 270 | |
| 49 | 283 | 295 | 307 | 320 | 332 | 345 | 357 | 370 | 382 | 394 | |
| 350 | 54 407 | 419 | 432 | 444 | 456 | 469 | 481 | 494 | 506 | 518 | |
| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |

15
1 1.5
2 3.0
3 4.5
4 6.0
5 7.5
6 9.0
7 10.5
8 12.0
9 13.5

14
1 1.4
2 2.8
3 4.2
4 5.6
5 7.0
6 8.4
7 9.8
8 11.2
9 12.6

13
1 1.3
2 2.6
3 3.9
4 5.2
5 6.5
6 7.8
7 9.1
8 10.4
9 11.7

12
1 1.2
2 2.4
3 3.6
4 4.8
5 6.0
6 7.2
7 8.4
8 9.6
9 10.8

| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|--|-----|--------|------|------|------|------|------|------|------|------|------|
| 13 1.3 2.6 3.9 5.2 6.5 7.8 9.1 10.4 11.7 | | 350 | 54 407 | 419 | 432 | 444 | 456 | 469 | 481 | 494 | 506 | 518 |
| | | 51 | 531 | 543 | 555 | 568 | 580 | 593 | 605 | 617 | 630 | 642 |
| | | 52 | 654 | 667 | 679 | 691 | 704 | 716 | 728 | 741 | 753 | 765 |
| | | 53 | 777 | 790 | 802 | 814 | 827 | 839 | 851 | 864 | 876 | 888 |
| | | 54 | 54 900 | 913 | 925 | 937 | 949 | 962 | 974 | 986 | 998 | *011 |
| | | 55 | 55 023 | 035 | 047 | 060 | 072 | 084 | 096 | 108 | 121 | 133 |
| | | 56 | 145 | 157 | 169 | 182 | 194 | 206 | 218 | 230 | 242 | 255 |
| | | 57 | 267 | 279 | 291 | 303 | 315 | 328 | 340 | 352 | 364 | 376 |
| | | 58 | 388 | 400 | 413 | 425 | 437 | 449 | 461 | 473 | 485 | 497 |
| | | 59 | 509 | 522 | 534 | 546 | 558 | 570 | 582 | 594 | 606 | 618 |
| 12 1.2 2.4 3.6 4.8 6.0 7.2 8.4 9.6 10.8 | | 360 | 630 | 642 | 654 | 666 | 678 | 691 | 703 | 715 | 727 | 739 |
| | | 61 | 751 | 763 | 775 | 787 | 799 | 811 | 823 | 835 | 847 | 859 |
| | | 62 | 871 | 883 | 895 | 907 | 919 | 931 | 943 | 955 | 967 | 979 |
| | | 63 | 55 991 | *003 | *015 | *027 | *038 | *050 | *062 | *074 | *086 | *098 |
| | | 64 | 56 110 | 122 | 134 | 146 | 158 | 170 | 182 | 194 | 205 | 217 |
| | | 65 | 229 | 241 | 253 | 265 | 277 | 289 | 301 | 312 | 324 | 336 |
| | | 66 | 348 | 360 | 372 | 384 | 396 | 407 | 419 | 431 | 443 | 455 |
| | | 67 | 467 | 478 | 490 | 502 | 514 | 526 | 538 | 549 | 561 | 573 |
| | | 68 | 585 | 597 | 608 | 620 | 632 | 644 | 656 | 667 | 679 | 691 |
| | | 69 | 703 | 714 | 726 | 738 | 750 | 761 | 773 | 785 | 797 | 808 |
| 11 1.1 2.2 3.3 4.4 5.5 6.6 7.7 8.8 9.9 | | 370 | 820 | 832 | 844 | 855 | 867 | 879 | 891 | 902 | 914 | 926 |
| | | 71 | 56 937 | 949 | 961 | 972 | 984 | 996 | *008 | *019 | *031 | *043 |
| | | 72 | 57 054 | 066 | 078 | 089 | 101 | 113 | 124 | 136 | 148 | 159 |
| | | 73 | 171 | 183 | 194 | 206 | 217 | 229 | 241 | 252 | 264 | 276 |
| | | 74 | 287 | 299 | 310 | 322 | 334 | 345 | 357 | 368 | 380 | 392 |
| | | 75 | 403 | 415 | 426 | 438 | 449 | 461 | 473 | 484 | 496 | 507 |
| | | 76 | 519 | 530 | 542 | 553 | 565 | 576 | 588 | 600 | 611 | 623 |
| | | 77 | 634 | 646 | 657 | 669 | 680 | 692 | 703 | 715 | 726 | 738 |
| | | 78 | 749 | 761 | 772 | 784 | 795 | 807 | 818 | 830 | 841 | 852 |
| | | 79 | 864 | 875 | 887 | 898 | 910 | 921 | 933 | 944 | 955 | 967 |
| 10 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 | | 380 | 57 978 | 990 | *001 | *013 | *024 | *035 | *047 | *058 | *070 | *081 |
| | | 81 | 58 092 | 104 | 115 | 127 | 138 | 149 | 161 | 172 | 184 | 195 |
| | | 82 | 206 | 218 | 229 | 240 | 252 | 263 | 274 | 286 | 297 | 309 |
| | | 83 | 320 | 331 | 343 | 354 | 365 | 377 | 388 | 399 | 410 | 422 |
| | | 84 | 433 | 444 | 456 | 467 | 478 | 490 | 501 | 512 | 524 | 535 |
| | | 85 | 546 | 557 | 569 | 580 | 591 | 602 | 614 | 625 | 636 | 647 |
| | | 86 | 659 | 670 | 681 | 692 | 704 | 715 | 726 | 737 | 749 | 760 |
| | | 87 | 771 | 782 | 794 | 805 | 816 | 827 | 838 | 850 | 861 | 872 |
| | | 88 | 883 | 894 | 906 | 917 | 928 | 939 | 950 | 961 | 973 | 984 |
| | | 89 | 58 995 | *006 | *017 | *028 | *040 | *051 | *062 | *073 | *084 | *095 |
| | | 390 | 59 106 | 118 | 129 | 140 | 151 | 162 | 173 | 184 | 195 | 207 |
| | | 91 | 218 | 229 | 240 | 251 | 262 | 273 | 284 | 295 | 306 | 318 |
| | | 92 | 329 | 340 | 351 | 362 | 373 | 384 | 395 | 406 | 417 | 428 |
| | | 93 | 439 | 450 | 461 | 472 | 483 | 494 | 506 | 517 | 528 | 539 |
| | | 94 | 550 | 561 | 572 | 583 | 594 | 605 | 616 | 627 | 638 | 649 |
| | | 95 | 660 | 671 | 682 | 693 | 704 | 715 | 726 | 737 | 748 | 759 |
| | | 96 | 770 | 780 | 791 | 802 | 813 | 824 | 835 | 846 | 857 | 868 |
| | | 97 | 879 | 890 | 901 | 912 | 923 | 934 | 945 | 956 | 966 | 977 |
| | | 98 | 59 988 | 999 | *010 | *021 | *032 | *043 | *054 | *065 | *076 | *086 |
| | | 99 | 60 097 | 108 | 119 | 130 | 141 | 152 | 163 | 173 | 184 | 195 |
| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |
|-----|--------|-----|-----|-----|------|------|------|------|------|------|--|
| 400 | 60 206 | 217 | 228 | 239 | 249 | 260 | 271 | 282 | 293 | 304 | <div>11</div> <div>1 1.1</div> <div>2 2.2</div> <div>3 3.3</div> <div>4 4.4</div> <div>5 5.5</div> <div>6 6.6</div> <div>7 7.7</div> <div>8 8.8</div> <div>9 9.9</div> |
| 01 | 314 | 325 | 336 | 347 | 358 | 369 | 379 | 390 | 401 | 412 | |
| 02 | 423 | 433 | 444 | 455 | 466 | 477 | 487 | 498 | 509 | 520 | |
| 03 | 531 | 541 | 552 | 563 | 574 | 584 | 595 | 606 | 617 | 627 | |
| 04 | 638 | 649 | 660 | 670 | 681 | 692 | 703 | 713 | 724 | 735 | |
| 05 | 746 | 756 | 767 | 778 | 788 | 799 | 810 | 821 | 831 | 842 | |
| 06 | 853 | 863 | 874 | 885 | 895 | 906 | 917 | 927 | 938 | 949 | |
| 07 | 60 959 | 970 | 981 | 991 | *002 | *013 | *023 | *034 | *045 | *055 | |
| 08 | 61 066 | 077 | 087 | 098 | 109 | 119 | 130 | 140 | 151 | 162 | |
| 09 | 172 | 183 | 194 | 204 | 215 | 225 | 236 | 247 | 257 | 268 | |
| 410 | 278 | 289 | 300 | 310 | 321 | 331 | 342 | 352 | 363 | 374 | <div>10</div> <div>1 1.0</div> <div>2 2.0</div> <div>3 3.0</div> <div>4 4.0</div> <div>5 5.0</div> <div>6 6.0</div> <div>7 7.0</div> <div>8 8.0</div> <div>9 9.0</div> |
| 11 | 384 | 395 | 405 | 416 | 426 | 437 | 448 | 458 | 469 | 479 | |
| 12 | 490 | 500 | 511 | 521 | 532 | 542 | 553 | 563 | 574 | 584 | |
| 13 | 595 | 606 | 616 | 627 | 637 | 648 | 658 | 669 | 679 | 690 | |
| 14 | 700 | 711 | 721 | 731 | 742 | 752 | 763 | 773 | 784 | 794 | |
| 15 | 805 | 815 | 826 | 836 | 847 | 857 | 868 | 878 | 888 | 899 | |
| 16 | 61 909 | 920 | 930 | 941 | 951 | 962 | 972 | 982 | 993 | *003 | |
| 17 | 62 014 | 024 | 034 | 045 | 055 | 066 | 076 | 086 | 097 | 107 | |
| 18 | 118 | 128 | 138 | 149 | 159 | 170 | 180 | 190 | 201 | 211 | |
| 19 | 221 | 232 | 242 | 252 | 263 | 273 | 284 | 294 | 304 | 315 | |
| 420 | 325 | 335 | 346 | 356 | 366 | 377 | 387 | 397 | 408 | 418 | <div>9</div> <div>1 0.9</div> <div>2 1.8</div> <div>3 2.7</div> <div>4 3.6</div> <div>5 4.5</div> <div>6 5.4</div> <div>7 6.3</div> <div>8 7.2</div> <div>9 8.1</div> |
| 21 | 428 | 439 | 449 | 459 | 469 | 480 | 490 | 500 | 511 | 521 | |
| 22 | 531 | 542 | 552 | 562 | 572 | 583 | 593 | 603 | 613 | 624 | |
| 23 | 634 | 644 | 655 | 665 | 675 | 685 | 696 | 706 | 716 | 726 | |
| 24 | 737 | 747 | 757 | 767 | 778 | 788 | 798 | 808 | 818 | 829 | |
| 25 | 839 | 849 | 859 | 870 | 880 | 890 | 900 | 910 | 921 | 931 | |
| 26 | 62 941 | 951 | 961 | 972 | 982 | 992 | *002 | *012 | *022 | *033 | |
| 27 | 63 043 | 053 | 063 | 073 | 083 | 094 | 104 | 114 | 124 | 134 | |
| 28 | 144 | 155 | 165 | 175 | 185 | 195 | 205 | 215 | 225 | 236 | |
| 29 | 246 | 256 | 266 | 276 | 286 | 296 | 306 | 316 | 327 | 337 | |
| 430 | 347 | 357 | 367 | 377 | 387 | 397 | 407 | 417 | 428 | 438 | <div>8</div> <div>1 0.8</div> <div>2 1.6</div> <div>3 2.4</div> <div>4 3.2</div> <div>5 4.0</div> <div>6 4.8</div> <div>7 5.6</div> <div>8 6.4</div> <div>9 7.2</div> |
| 31 | 448 | 458 | 468 | 478 | 488 | 498 | 508 | 518 | 528 | 538 | |
| 32 | 548 | 558 | 568 | 579 | 589 | 599 | 609 | 619 | 629 | 639 | |
| 33 | 649 | 659 | 669 | 679 | 689 | 699 | 709 | 719 | 729 | 739 | |
| 34 | 749 | 759 | 769 | 779 | 789 | 799 | 809 | 819 | 829 | 839 | |
| 35 | 849 | 859 | 869 | 879 | 889 | 899 | 909 | 919 | 929 | 939 | |
| 36 | 63 949 | 959 | 969 | 979 | 988 | 998 | *008 | *018 | *028 | *038 | |
| 37 | 64 048 | 058 | 068 | 078 | 088 | 098 | 108 | 118 | 128 | 137 | |
| 38 | 147 | 157 | 167 | 177 | 187 | 197 | 207 | 217 | 227 | 237 | |
| 39 | 246 | 256 | 266 | 276 | 286 | 296 | 306 | 316 | 326 | 335 | |
| 440 | 345 | 355 | 365 | 375 | 385 | 395 | 404 | 414 | 424 | 434 | <div>7</div> <div>1 0.7</div> <div>2 1.4</div> <div>3 2.1</div> <div>4 2.8</div> <div>5 3.5</div> <div>6 4.2</div> <div>7 4.9</div> <div>8 5.6</div> <div>9 6.3</div> |
| 41 | 444 | 454 | 464 | 473 | 483 | 493 | 503 | 513 | 523 | 532 | |
| 42 | 542 | 552 | 562 | 572 | 582 | 591 | 601 | 611 | 621 | 631 | |
| 43 | 640 | 650 | 660 | 670 | 680 | 689 | 699 | 709 | 719 | 729 | |
| 44 | 738 | 748 | 758 | 768 | 777 | 787 | 797 | 807 | 816 | 826 | |
| 45 | 836 | 846 | 856 | 865 | 875 | 885 | 895 | 904 | 914 | 924 | |
| 46 | 64 933 | 943 | 953 | 963 | 972 | 982 | 992 | *002 | *011 | *021 | |
| 47 | 65 031 | 040 | 050 | 060 | 070 | 079 | 089 | 099 | 108 | 118 | |
| 48 | 128 | 137 | 147 | 157 | 167 | 176 | 186 | 196 | 205 | 215 | |
| 49 | 225 | 234 | 244 | 254 | 263 | 273 | 283 | 292 | 302 | 312 | |
| 450 | 65 321 | 331 | 341 | 350 | 360 | 369 | 379 | 389 | 398 | 408 | Prop. Parts |
| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |

| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|--|-----|--------|------|------|------|------|------|------|------|------|------|
| 10 1 1.0 2 2.0 3 3.0 4 4.0 5 5.0 6 6.0 7 7.0 8 8.0 9 9.0 | | 450 | 65 321 | 331 | 341 | 350 | 360 | 369 | 379 | 389 | 398 | 408 |
| | | 51 | 418 | 427 | 437 | 447 | 456 | 466 | 475 | 485 | 495 | 504 |
| | | 52 | 514 | 523 | 533 | 543 | 552 | 562 | 571 | 581 | 591 | 600 |
| | | 53 | 610 | 619 | 629 | 639 | 648 | 658 | 667 | 677 | 686 | 696 |
| | | 54 | 706 | 715 | 725 | 734 | 744 | 753 | 763 | 772 | 782 | 792 |
| | | 55 | 801 | 811 | 820 | 830 | 839 | 849 | 858 | 868 | 877 | 887 |
| | | 56 | 896 | 906 | 916 | 925 | 935 | 944 | 954 | 963 | 973 | 982 |
| | | 57 | 65 992 | *001 | *011 | *020 | *030 | *039 | *049 | *058 | *068 | *077 |
| | | 58 | 66 087 | 096 | 106 | 115 | 124 | 134 | 143 | 153 | 162 | 172 |
| | | 59 | 181 | 191 | 200 | 210 | 219 | 229 | 238 | 247 | 257 | 266 |
| 9 7 7.0 8 8.0 9 9.0 | | 460 | 276 | 285 | 295 | 304 | 314 | 323 | 332 | 342 | 351 | 361 |
| | | 61 | 370 | 380 | 389 | 398 | 408 | 417 | 427 | 436 | 445 | 455 |
| | | 62 | 464 | 474 | 483 | 492 | 502 | 511 | 521 | 530 | 539 | 549 |
| | | 63 | 558 | 567 | 577 | 586 | 596 | 605 | 614 | 624 | 633 | 642 |
| | | 64 | 652 | 661 | 671 | 680 | 689 | 699 | 708 | 717 | 727 | 736 |
| | | 65 | 745 | 755 | 764 | 773 | 783 | 792 | 801 | 811 | 820 | 829 |
| | | 66 | 839 | 848 | 857 | 867 | 876 | 885 | 894 | 904 | 913 | 922 |
| | | 67 | 66 932 | 941 | 950 | 960 | 969 | 978 | 987 | 997 | *006 | *015 |
| | | 68 | 67 025 | 034 | 043 | 052 | 062 | 071 | 080 | 089 | 099 | 108 |
| | | 69 | 117 | 127 | 136 | 145 | 154 | 164 | 173 | 182 | 191 | 201 |
| 9 1 0.9 2 1.8 3 2.7 4 3.6 5 4.5 6 5.4 7 6.3 8 7.2 9 8.1 | | 470 | 210 | 219 | 228 | 237 | 247 | 256 | 265 | 274 | 284 | 293 |
| | | 71 | 302 | 311 | 321 | 330 | 339 | 348 | 357 | 367 | 376 | 385 |
| | | 72 | 394 | 403 | 413 | 422 | 431 | 440 | 449 | 459 | 468 | 477 |
| | | 73 | 486 | 495 | 504 | 514 | 523 | 532 | 541 | 550 | 560 | 569 |
| | | 74 | 578 | 587 | 596 | 605 | 614 | 624 | 633 | 642 | 651 | 660 |
| | | 75 | 669 | 679 | 688 | 697 | 706 | 715 | 724 | 733 | 742 | 752 |
| | | 76 | 761 | 770 | 779 | 788 | 797 | 806 | 815 | 825 | 834 | 843 |
| | | 77 | 852 | 861 | 870 | 879 | 888 | 897 | 906 | 916 | 925 | 934 |
| | | 78 | 67 943 | 952 | 961 | 970 | 979 | 988 | 997 | *006 | *015 | *024 |
| | | 79 | 68 034 | 043 | 052 | 061 | 070 | 079 | 088 | 097 | 106 | 115 |
| 8 1 0.8 2 1.6 3 2.4 4 3.2 5 4.0 6 4.8 7 5.6 8 6.4 9 7.2 | | 480 | 124 | 133 | 142 | 151 | 160 | 169 | 178 | 187 | 196 | 205 |
| | | 81 | 215 | 224 | 233 | 242 | 251 | 260 | 269 | 278 | 287 | 296 |
| | | 82 | 305 | 314 | 323 | 332 | 341 | 350 | 359 | 368 | 377 | 386 |
| | | 83 | 395 | 404 | 413 | 422 | 431 | 440 | 449 | 458 | 467 | 476 |
| | | 84 | 485 | 494 | 502 | 511 | 520 | 529 | 538 | 547 | 556 | 565 |
| | | 85 | 574 | 583 | 592 | 601 | 610 | 619 | 628 | 637 | 646 | 655 |
| | | 86 | 664 | 673 | 681 | 690 | 699 | 708 | 717 | 726 | 735 | 744 |
| | | 87 | 753 | 762 | 771 | 780 | 789 | 797 | 806 | 815 | 824 | 833 |
| | | 88 | 842 | 851 | 860 | 869 | 878 | 886 | 895 | 904 | 913 | 922 |
| | | 89 | 68 931 | 940 | 949 | 958 | 966 | 975 | 984 | 993 | *002 | *011 |
| 8 1 0.8 2 1.6 3 2.4 4 3.2 5 4.0 6 4.8 7 5.6 8 6.4 9 7.2 | | 490 | 69 020 | 028 | 037 | 046 | 055 | 064 | 073 | 082 | 090 | 099 |
| | | 91 | 108 | 117 | 126 | 135 | 144 | 152 | 161 | 170 | 179 | 188 |
| | | 92 | 197 | 205 | 214 | 223 | 232 | 241 | 249 | 258 | 267 | 276 |
| | | 93 | 285 | 294 | 302 | 311 | 320 | 329 | 338 | 346 | 355 | 364 |
| | | 94 | 373 | 381 | 390 | 399 | 408 | 417 | 425 | 434 | 443 | 452 |
| | | 95 | 461 | 469 | 478 | 487 | 496 | 504 | 513 | 522 | 531 | 539 |
| | | 96 | 548 | 557 | 566 | 574 | 583 | 592 | 601 | 609 | 618 | 627 |
| | | 97 | 636 | 644 | 653 | 662 | 671 | 679 | 688 | 697 | 705 | 714 |
| | | 98 | 723 | 732 | 740 | 749 | 758 | 767 | 775 | 784 | 793 | 801 |
| | | 99 | 810 | 819 | 827 | 836 | 845 | 854 | 862 | 871 | 880 | 888 |
| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |
|-----|--------|------|------|------|------|------|------|------|------|------|-------------|
| 500 | 69 897 | 906 | 914 | 923 | 932 | 940 | 949 | 958 | 966 | 975 | |
| 01 | 69 984 | 992 | *001 | *010 | *018 | *027 | *036 | *044 | *053 | *062 | |
| 02 | 70 070 | 079 | 088 | 096 | 105 | 114 | 122 | 131 | 140 | 148 | |
| 03 | 157 | 165 | 174 | 183 | 191 | 200 | 209 | 217 | 226 | 234 | |
| 04 | 243 | 252 | 260 | 269 | 278 | 286 | 295 | 303 | 312 | 321 | |
| 05 | 329 | 338 | 346 | 355 | 364 | 372 | 381 | 389 | 398 | 406 | |
| 06 | 415 | 424 | 432 | 441 | 449 | 458 | 467 | 475 | 484 | 492 | |
| 07 | 501 | 509 | 518 | 526 | 535 | 544 | 552 | 561 | 569 | 578 | |
| 08 | 586 | 595 | 603 | 612 | 621 | 629 | 638 | 646 | 655 | 663 | |
| 09 | 672 | 680 | 689 | 697 | 706 | 714 | 723 | 731 | 740 | 749 | |
| 510 | 757 | 766 | 774 | 783 | 791 | 800 | 808 | 817 | 825 | 834 | |
| 11 | 842 | 851 | 859 | 868 | 876 | 885 | 893 | 902 | 910 | 919 | |
| 12 | 70 927 | 935 | 944 | 952 | 961 | 969 | 978 | 986 | 995 | *003 | |
| 13 | 71 012 | 020 | 029 | 037 | 046 | 054 | 063 | 071 | 079 | 088 | |
| 14 | 096 | 105 | 113 | 122 | 130 | 139 | 147 | 155 | 164 | 172 | |
| 15 | 181 | 189 | 198 | 206 | 214 | 223 | 231 | 240 | 248 | 257 | |
| 16 | 265 | 273 | 282 | 290 | 299 | 307 | 315 | 324 | 332 | 341 | |
| 17 | 349 | 357 | 366 | 374 | 383 | 391 | 399 | 408 | 416 | 425 | |
| 18 | 433 | 441 | 450 | 458 | 466 | 475 | 483 | 492 | 500 | 508 | |
| 19 | 517 | 525 | 533 | 542 | 550 | 559 | 567 | 575 | 584 | 592 | |
| 520 | 600 | 609 | 617 | 625 | 634 | 642 | 650 | 659 | 667 | 675 | |
| 21 | 684 | 692 | 700 | 709 | 717 | 725 | 734 | 742 | 750 | 759 | |
| 22 | 767 | 775 | 784 | 792 | 800 | 809 | 817 | 825 | 834 | 842 | |
| 23 | 850 | 858 | 867 | 875 | 883 | 892 | 900 | 908 | 917 | 925 | |
| 24 | 71 933 | 941 | 950 | 958 | 966 | 975 | 983 | 991 | 999 | *008 | |
| 25 | 72 016 | 024 | 032 | 041 | 049 | 057 | 066 | 074 | 082 | 090 | |
| 26 | 099 | 107 | 115 | 123 | 132 | 140 | 148 | 156 | 165 | 173 | |
| 27 | 181 | 189 | 198 | 206 | 214 | 222 | 230 | 239 | 247 | 255 | |
| 28 | 263 | 272 | 280 | 288 | 296 | 304 | 313 | 321 | 329 | 337 | |
| 29 | 346 | 354 | 362 | 370 | 378 | 387 | 395 | 403 | 411 | 419 | |
| 530 | 428 | 436 | 444 | 452 | 460 | 469 | 477 | 485 | 493 | 501 | |
| 31 | 509 | 518 | 526 | 534 | 542 | 550 | 558 | 567 | 575 | 583 | |
| 32 | 591 | 599 | 607 | 616 | 624 | 632 | 640 | 648 | 656 | 665 | |
| 33 | 673 | 681 | 689 | 697 | 705 | 713 | 722 | 730 | 738 | 746 | |
| 34 | 754 | 762 | 770 | 779 | 787 | 795 | 803 | 811 | 819 | 827 | |
| 35 | 835 | 843 | 852 | 860 | 868 | 876 | 884 | 892 | 900 | 908 | |
| 36 | 916 | 925 | 933 | 941 | 949 | 957 | 965 | 973 | 981 | 989 | |
| 37 | 72 997 | *006 | *014 | *022 | *030 | *038 | *046 | *054 | *062 | *070 | |
| 38 | 73 078 | 086 | 094 | 102 | 111 | 119 | 127 | 135 | 143 | 151 | |
| 39 | 159 | 167 | 175 | 183 | 191 | 199 | 207 | 215 | 223 | 231 | |
| 540 | 239 | 247 | 255 | 263 | 272 | 280 | 288 | 296 | 304 | 312 | |
| 41 | 320 | 328 | 336 | 344 | 352 | 360 | 368 | 376 | 384 | 392 | |
| 42 | 400 | 408 | 416 | 424 | 432 | 440 | 448 | 456 | 464 | 472 | |
| 43 | 480 | 488 | 496 | 504 | 512 | 520 | 528 | 536 | 544 | 552 | |
| 44 | 560 | 568 | 576 | 584 | 592 | 600 | 608 | 616 | 624 | 632 | |
| 45 | 640 | 648 | 656 | 664 | 672 | 679 | 687 | 695 | 703 | 711 | |
| 46 | 719 | 727 | 735 | 743 | 751 | 759 | 767 | 775 | 783 | 791 | |
| 47 | 799 | 807 | 815 | 823 | 830 | 838 | 846 | 854 | 862 | 870 | |
| 48 | 878 | 886 | 894 | 902 | 910 | 918 | 926 | 933 | 941 | 949 | |
| 49 | 73 957 | 965 | 973 | 981 | 989 | 997 | *005 | *013 | *020 | *028 | |
| 550 | 74 036 | 044 | 052 | 060 | 068 | 076 | 084 | 092 | 099 | 107 | |
| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |

9
1 0.9
2 1.8
3 2.7
4 3.6
5 4.5
6 5.4
7 6.3
8 7.2
9 8.1

8
1 0.8
2 1.6
3 2.4
4 3.2
5 4.0
6 4.8
7 5.6
8 6.4
9 7.2

7
1 0.7
2 1.4
3 2.1
4 2.8
5 3.5
6 4.2
7 4.9
8 5.6
9 6.3

| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|-----|-----|--------|-----|-----|-----|------|------|------|------|------|------|
| | | 550 | 74 036 | 044 | 052 | 060 | 068 | 076 | 084 | 092 | 099 | 107 |
| | | 51 | 115 | 123 | 131 | 139 | 147 | 155 | 162 | 170 | 178 | 186 |
| | | 52 | 194 | 202 | 210 | 218 | 225 | 233 | 241 | 249 | 257 | 265 |
| | | 53 | 273 | 280 | 288 | 296 | 304 | 312 | 320 | 327 | 335 | 343 |
| | | 54 | 351 | 359 | 367 | 374 | 382 | 390 | 398 | 406 | 414 | 421 |
| | | 55 | 429 | 437 | 445 | 453 | 461 | 468 | 476 | 484 | 492 | 500 |
| | | 56 | 507 | 515 | 523 | 531 | 539 | 547 | 554 | 562 | 570 | 578 |
| | | 57 | 586 | 593 | 601 | 609 | 617 | 624 | 632 | 640 | 648 | 656 |
| | | 58 | 663 | 671 | 679 | 687 | 695 | 702 | 710 | 718 | 726 | 733 |
| | | 59 | 741 | 749 | 757 | 764 | 772 | 780 | 788 | 796 | 803 | 811 |
| | | 560 | 819 | 827 | 834 | 842 | 850 | 858 | 865 | 873 | 881 | 889 |
| 1 2 3 4 5 6 7 8 9 | 8 | 61 | 896 | 904 | 912 | 920 | 927 | 935 | 943 | 950 | 958 | 966 |
| | | 62 | 74 974 | 981 | 989 | 997 | *005 | *012 | *020 | *028 | *035 | *043 |
| | 0.8 | 63 | 75 051 | 059 | 066 | 074 | 082 | 089 | 097 | 105 | 113 | 120 |
| | 1.6 | 64 | 128 | 136 | 143 | 151 | 159 | 166 | 174 | 182 | 189 | 197 |
| | 2.4 | 65 | 205 | 213 | 220 | 228 | 236 | 243 | 251 | 259 | 266 | 274 |
| | 3.2 | 66 | 282 | 289 | 297 | 305 | 312 | 320 | 328 | 335 | 343 | 351 |
| | 4.0 | 67 | 358 | 366 | 374 | 381 | 389 | 397 | 404 | 412 | 420 | 427 |
| | 4.8 | 68 | 435 | 442 | 450 | 458 | 465 | 473 | 481 | 488 | 496 | 504 |
| | 5.6 | 69 | 511 | 519 | 526 | 534 | 542 | 549 | 557 | 565 | 572 | 580 |
| | 6.4 | | | | | | | | | | | |
| | 7.2 | | | | | | | | | | | |
| | | 570 | 587 | 595 | 603 | 610 | 618 | 626 | 633 | 641 | 648 | 656 |
| | | 71 | 664 | 671 | 679 | 686 | 694 | 702 | 709 | 717 | 724 | 732 |
| | | 72 | 740 | 747 | 755 | 762 | 770 | 778 | 785 | 793 | 800 | 808 |
| | | 73 | 815 | 823 | 831 | 838 | 846 | 853 | 861 | 868 | 876 | 884 |
| | | 74 | 891 | 899 | 906 | 914 | 921 | 929 | 937 | 944 | 952 | 959 |
| | | 75 | 75 967 | 974 | 982 | 989 | 997 | *005 | *012 | *020 | *028 | *035 |
| | | 76 | 76 042 | 050 | 057 | 065 | 072 | 080 | 087 | 095 | 103 | 110 |
| | | 77 | 118 | 125 | 133 | 140 | 148 | 155 | 163 | 170 | 178 | 185 |
| | | 78 | 193 | 200 | 208 | 215 | 223 | 230 | 238 | 245 | 253 | 260 |
| | | 79 | 268 | 275 | 283 | 290 | 298 | 305 | 313 | 320 | 328 | 335 |
| | | 580 | 343 | 350 | 358 | 365 | 373 | 380 | 388 | 395 | 403 | 410 |
| 1 2 3 4 5 6 7 8 9 | 7 | 81 | 418 | 425 | 433 | 440 | 448 | 455 | 462 | 470 | 477 | 485 |
| | | 82 | 492 | 500 | 507 | 515 | 522 | 530 | 537 | 545 | 552 | 559 |
| | 0.7 | 83 | 567 | 574 | 582 | 589 | 597 | 604 | 612 | 619 | 626 | 634 |
| | 1.4 | 84 | 641 | 649 | 656 | 664 | 671 | 678 | 686 | 693 | 701 | 708 |
| | 2.1 | 85 | 716 | 723 | 730 | 738 | 745 | 753 | 760 | 768 | 775 | 782 |
| | 2.8 | 86 | 790 | 797 | 805 | 812 | 819 | 827 | 834 | 842 | 849 | 856 |
| | 3.5 | 87 | 864 | 871 | 879 | 886 | 893 | 901 | 908 | 916 | 923 | 930 |
| | 4.2 | 88 | 76 938 | 945 | 953 | 960 | 967 | 975 | 982 | 989 | 997 | *004 |
| | 4.9 | 89 | 77 012 | 019 | 026 | 034 | 041 | 048 | 056 | 063 | 070 | 078 |
| | 5.6 | | | | | | | | | | | |
| | 6.3 | | | | | | | | | | | |
| | | 590 | 085 | 093 | 100 | 107 | 115 | 122 | 129 | 137 | 144 | 151 |
| | | 91 | 159 | 166 | 173 | 181 | 188 | 195 | 203 | 210 | 217 | 225 |
| | | 92 | 232 | 240 | 247 | 254 | 262 | 269 | 276 | 283 | 291 | 298 |
| | | 93 | 305 | 313 | 320 | 327 | 335 | 342 | 349 | 357 | 364 | 371 |
| | | 94 | 379 | 386 | 393 | 401 | 408 | 415 | 422 | 430 | 437 | 444 |
| | | 95 | 452 | 459 | 466 | 474 | 481 | 488 | 495 | 503 | 510 | 517 |
| | | 96 | 525 | 532 | 539 | 546 | 554 | 561 | 568 | 576 | 583 | 590 |
| | | 97 | 597 | 605 | 612 | 619 | 627 | 634 | 641 | 648 | 656 | 663 |
| | | 98 | 670 | 677 | 685 | 692 | 699 | 706 | 714 | 721 | 728 | 735 |
| | | 99 | 743 | 750 | 757 | 764 | 772 | 779 | 786 | 793 | 801 | 808 |
| | | 600 | 77 815 | 822 | 830 | 837 | 844 | 851 | 859 | 866 | 873 | 880 |
| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |
|-----|--------|-----|-----|-----|-----|-----|------|------|------|------|-------------|
| 600 | 77 815 | 822 | 830 | 837 | 844 | 851 | 859 | 866 | 873 | 880 | |
| 01 | 887 | 895 | 902 | 909 | 916 | 924 | 931 | 938 | 945 | 952 | |
| 02 | 77 960 | 967 | 974 | 981 | 988 | 996 | *003 | *010 | *017 | *025 | |
| 03 | 78 032 | 039 | 046 | 053 | 061 | 068 | 075 | 082 | 089 | 097 | |
| 04 | 104 | 111 | 118 | 125 | 132 | 140 | 147 | 154 | 161 | 168 | |
| 05 | 176 | 183 | 190 | 197 | 204 | 211 | 219 | 226 | 233 | 240 | |
| 06 | 247 | 254 | 262 | 269 | 276 | 283 | 290 | 297 | 305 | 312 | |
| 07 | 319 | 326 | 333 | 340 | 347 | 355 | 362 | 369 | 376 | 383 | |
| 08 | 390 | 398 | 405 | 412 | 419 | 426 | 433 | 440 | 447 | 455 | |
| 09 | 462 | 469 | 476 | 483 | 490 | 497 | 504 | 512 | 519 | 526 | |
| 610 | 533 | 540 | 547 | 554 | 561 | 569 | 576 | 583 | 590 | 597 | |
| 11 | 604 | 611 | 618 | 625 | 633 | 640 | 647 | 654 | 661 | 668 | |
| 12 | 675 | 682 | 689 | 696 | 704 | 711 | 718 | 725 | 732 | 739 | |
| 13 | 746 | 753 | 760 | 767 | 774 | 781 | 789 | 796 | 803 | 810 | |
| 14 | 817 | 824 | 831 | 838 | 845 | 852 | 859 | 866 | 873 | 880 | |
| 15 | 888 | 895 | 902 | 909 | 916 | 923 | 930 | 937 | 944 | 951 | |
| 16 | 78 958 | 965 | 972 | 979 | 986 | 993 | *000 | *007 | *014 | *021 | |
| 17 | 79 029 | 036 | 043 | 050 | 057 | 064 | 071 | 078 | 085 | 092 | |
| 18 | 099 | 106 | 113 | 120 | 127 | 134 | 141 | 148 | 155 | 162 | |
| 19 | 169 | 176 | 183 | 190 | 197 | 204 | 211 | 218 | 225 | 232 | |
| 620 | 239 | 246 | 253 | 260 | 267 | 274 | 281 | 288 | 295 | 302 | |
| 21 | 309 | 316 | 323 | 330 | 337 | 344 | 351 | 358 | 365 | 372 | |
| 22 | 379 | 386 | 393 | 400 | 407 | 414 | 421 | 428 | 435 | 442 | |
| 23 | 449 | 456 | 463 | 470 | 477 | 484 | 491 | 498 | 505 | 511 | |
| 24 | 518 | 525 | 532 | 539 | 546 | 553 | 560 | 567 | 574 | 581 | |
| 25 | 588 | 595 | 602 | 609 | 616 | 623 | 630 | 637 | 644 | 650 | |
| 26 | 657 | 664 | 671 | 678 | 685 | 692 | 699 | 706 | 713 | 720 | |
| 27 | 727 | 734 | 741 | 748 | 754 | 761 | 768 | 775 | 782 | 789 | |
| 28 | 796 | 803 | 810 | 817 | 824 | 831 | 837 | 844 | 851 | 858 | |
| 29 | 865 | 872 | 879 | 886 | 893 | 900 | 906 | 913 | 920 | 927 | |
| 630 | 79 934 | 941 | 948 | 955 | 962 | 969 | 976 | 982 | 989 | 996 | |
| 31 | 80 003 | 010 | 017 | 024 | 030 | 037 | 044 | 051 | 058 | 065 | |
| 32 | 072 | 079 | 085 | 092 | 099 | 106 | 113 | 120 | 127 | 134 | |
| 33 | 140 | 147 | 154 | 161 | 168 | 175 | 182 | 188 | 195 | 202 | |
| 34 | 209 | 216 | 223 | 229 | 236 | 243 | 250 | 257 | 264 | 271 | |
| 35 | 277 | 284 | 291 | 298 | 305 | 312 | 318 | 325 | 332 | 339 | |
| 36 | 346 | 353 | 359 | 366 | 373 | 380 | 387 | 393 | 400 | 407 | |
| 37 | 414 | 421 | 428 | 434 | 441 | 448 | 455 | 462 | 468 | 475 | |
| 38 | 482 | 489 | 496 | 502 | 509 | 516 | 523 | 530 | 536 | 543 | |
| 39 | 550 | 557 | 564 | 570 | 577 | 584 | 591 | 598 | 604 | 611 | |
| 640 | 618 | 625 | 632 | 638 | 645 | 652 | 659 | 665 | 672 | 679 | |
| 41 | 686 | 693 | 699 | 706 | 713 | 720 | 726 | 733 | 740 | 747 | |
| 42 | 754 | 760 | 767 | 774 | 781 | 787 | 794 | 801 | 808 | 814 | |
| 43 | 821 | 828 | 835 | 841 | 848 | 855 | 862 | 868 | 875 | 882 | |
| 44 | 889 | 895 | 902 | 909 | 916 | 922 | 929 | 936 | 943 | 949 | |
| 45 | 80 956 | 963 | 969 | 976 | 983 | 990 | 996 | *003 | *010 | *017 | |
| 46 | 81 023 | 030 | 037 | 043 | 050 | 057 | 064 | 070 | 077 | 084 | |
| 47 | 090 | 097 | 104 | 111 | 117 | 124 | 131 | 137 | 144 | 151 | |
| 48 | 158 | 164 | 171 | 178 | 184 | 191 | 198 | 204 | 211 | 218 | |
| 49 | 224 | 231 | 238 | 245 | 251 | 258 | 265 | 271 | 278 | 285 | |
| 650 | 81 291 | 298 | 305 | 311 | 318 | 325 | 331 | 338 | 345 | 351 | |
| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |

8
1 0.8
2 1.6
3 2.4
4 3.2
5 4.0
6 4.8
7 5.6
8 6.4
9 7.2

7
1 0.7
2 1.4
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4 2.8
5 3.5
6 4.2
7 4.9
8 5.6
9 6.3

6
1 0.6
2 1.2
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4 2.4
5 3.0
6 3.6
7 4.2
8 4.8
9 5.4

| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|--|--|-----|--------|------|------|------|------|------|------|------|------|------|
| <div> <div>7</div> <div>1 0.7</div> <div>2 1.4</div> <div>3 2.1</div> <div>4 2.8</div> <div>5 3.5</div> <div>6 4.2</div> <div>7 4.9</div> <div>8 5.6</div> <div>9 6.3</div> </div> | | 650 | 81 291 | 298 | 305 | 311 | 318 | 325 | 331 | 338 | 345 | 351 |
| | | 51 | 358 | 365 | 371 | 378 | 385 | 391 | 398 | 405 | 411 | 418 |
| | | 52 | 425 | 431 | 438 | 445 | 451 | 458 | 465 | 471 | 478 | 485 |
| | | 53 | 491 | 498 | 505 | 511 | 518 | 525 | 531 | 538 | 544 | 551 |
| | | 54 | 558 | 564 | 571 | 578 | 584 | 591 | 598 | 604 | 611 | 617 |
| | | 55 | 624 | 631 | 637 | 644 | 651 | 657 | 664 | 671 | 677 | 684 |
| | | 56 | 690 | 697 | 704 | 710 | 717 | 723 | 730 | 737 | 743 | 750 |
| | | 57 | 757 | 763 | 770 | 776 | 783 | 790 | 796 | 803 | 809 | 816 |
| | | 58 | 823 | 829 | 836 | 842 | 849 | 856 | 862 | 869 | 875 | 882 |
| | | 59 | 889 | 895 | 902 | 908 | 915 | 921 | 928 | 935 | 941 | 948 |
| | | 660 | 81 954 | 961 | 968 | 974 | 981 | 987 | 994 | *000 | *007 | *014 |
| | | 61 | 82 020 | 027 | 033 | 040 | 046 | 053 | 060 | 066 | 073 | 079 |
| | | 62 | 086 | 092 | 099 | 105 | 112 | 119 | 125 | 132 | 138 | 145 |
| | | 63 | 151 | 158 | 164 | 171 | 178 | 184 | 191 | 197 | 204 | 210 |
| | | 64 | 217 | 223 | 230 | 236 | 243 | 249 | 256 | 263 | 269 | 276 |
| | | 65 | 282 | 289 | 295 | 302 | 308 | 315 | 321 | 328 | 334 | 341 |
| | | 66 | 347 | 354 | 360 | 367 | 373 | 380 | 387 | 393 | 400 | 406 |
| | | 67 | 413 | 419 | 426 | 432 | 439 | 445 | 452 | 458 | 465 | 471 |
| | | 68 | 478 | 484 | 491 | 497 | 504 | 510 | 517 | 523 | 530 | 536 |
| | | 69 | 543 | 549 | 556 | 562 | 569 | 575 | 582 | 588 | 595 | 601 |
| | | 670 | 607 | 614 | 620 | 627 | 633 | 640 | 646 | 653 | 659 | 666 |
| | | 71 | 672 | 679 | 685 | 692 | 698 | 705 | 711 | 718 | 724 | 730 |
| | | 72 | 737 | 743 | 750 | 756 | 763 | 769 | 776 | 782 | 789 | 795 |
| | | 73 | 802 | 808 | 814 | 821 | 827 | 834 | 840 | 847 | 853 | 860 |
| | | 74 | 866 | 872 | 879 | 885 | 892 | 898 | 905 | 911 | 918 | 924 |
| | | 75 | 930 | 937 | 943 | 950 | 956 | 963 | 969 | 975 | 982 | 988 |
| | | 76 | 82 995 | *001 | *008 | *014 | *020 | *027 | *033 | *040 | *046 | *052 |
| | | 77 | 83 059 | 065 | 072 | 078 | 085 | 091 | 097 | 104 | 110 | 117 |
| | | 78 | 123 | 129 | 136 | 142 | 149 | 155 | 161 | 168 | 174 | 181 |
| | | 79 | 187 | 193 | 200 | 206 | 213 | 219 | 225 | 232 | 238 | 245 |
| <div> <div>6</div> <div>1 0.6</div> <div>2 1.2</div> <div>3 1.8</div> <div>4 2.4</div> <div>5 3.0</div> <div>6 3.6</div> <div>7 4.2</div> <div>8 4.8</div> <div>9 5.4</div> </div> | | 680 | 251 | 257 | 264 | 270 | 276 | 283 | 289 | 296 | 302 | 308 |
| | | 81 | 315 | 321 | 327 | 334 | 340 | 347 | 353 | 359 | 366 | 372 |
| | | 82 | 378 | 385 | 391 | 398 | 404 | 410 | 417 | 423 | 429 | 436 |
| | | 83 | 442 | 448 | 455 | 461 | 467 | 474 | 480 | 487 | 493 | 499 |
| | | 84 | 506 | 512 | 518 | 525 | 531 | 537 | 544 | 550 | 556 | 563 |
| | | 85 | 569 | 575 | 582 | 588 | 594 | 601 | 607 | 613 | 620 | 626 |
| | | 86 | 632 | 639 | 645 | 651 | 658 | 664 | 670 | 677 | 683 | 689 |
| | | 87 | 696 | 702 | 708 | 715 | 721 | 727 | 734 | 740 | 746 | 753 |
| | | 88 | 759 | 765 | 771 | 778 | 784 | 790 | 797 | 803 | 809 | 816 |
| | | 89 | 822 | 828 | 835 | 841 | 847 | 853 | 860 | 866 | 872 | 879 |
| | | 690 | 885 | 891 | 897 | 904 | 910 | 916 | 923 | 929 | 935 | 942 |
| | | 91 | 83 948 | 954 | 960 | 967 | 973 | 979 | 985 | 992 | 998 | *004 |
| | | 92 | 84 011 | 017 | 023 | 029 | 036 | 042 | 048 | 055 | 061 | 067 |
| | | 93 | 073 | 080 | 086 | 092 | 098 | 105 | 111 | 117 | 123 | 130 |
| | | 94 | 136 | 142 | 148 | 155 | 161 | 167 | 173 | 180 | 186 | 192 |
| | | 95 | 198 | 205 | 211 | 217 | 223 | 230 | 236 | 242 | 248 | 255 |
| | | 96 | 261 | 267 | 273 | 280 | 286 | 292 | 298 | 305 | 311 | 317 |
| | | 97 | 323 | 330 | 336 | 342 | 348 | 354 | 361 | 367 | 373 | 379 |
| | | 98 | 386 | 392 | 398 | 404 | 410 | 417 | 423 | 429 | 435 | 442 |
| | | 99 | 448 | 454 | 460 | 466 | 473 | 479 | 485 | 491 | 497 | 504 |
| | | 700 | 84 510 | 516 | 522 | 528 | 535 | 541 | 547 | 553 | 559 | 566 |
| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |
|-----|--------|-----|-----|-----|------|------|------|------|------|------|-------------|
| 700 | 84 510 | 516 | 522 | 528 | 535 | 541 | 547 | 553 | 559 | 566 | |
| 01 | 572 | 578 | 584 | 590 | 597 | 603 | 609 | 615 | 621 | 628 | |
| 02 | 634 | 640 | 646 | 652 | 658 | 665 | 671 | 677 | 683 | 689 | |
| 03 | 696 | 702 | 708 | 714 | 720 | 726 | 733 | 739 | 745 | 751 | |
| 04 | 757 | 763 | 770 | 776 | 782 | 788 | 794 | 800 | 807 | 813 | |
| 05 | 819 | 825 | 831 | 837 | 844 | 850 | 856 | 862 | 868 | 874 | |
| 06 | 880 | 887 | 893 | 899 | 905 | 911 | 917 | 924 | 930 | 936 | |
| 07 | 84 942 | 948 | 954 | 960 | 967 | 973 | 979 | 985 | 991 | 997 | |
| 08 | 85 003 | 009 | 016 | 022 | 028 | 034 | 040 | 046 | 052 | 058 | |
| 09 | 065 | 071 | 077 | 083 | 089 | 095 | 101 | 107 | 114 | 120 | |
| 710 | 126 | 132 | 138 | 144 | 150 | 156 | 163 | 169 | 175 | 181 | |
| 11 | 187 | 193 | 199 | 205 | 211 | 217 | 224 | 230 | 236 | 242 | |
| 12 | 248 | 254 | 260 | 266 | 272 | 278 | 285 | 291 | 297 | 303 | |
| 13 | 309 | 315 | 321 | 327 | 333 | 339 | 345 | 352 | 358 | 364 | |
| 14 | 370 | 376 | 382 | 388 | 394 | 400 | 406 | 412 | 418 | 425 | |
| 15 | 431 | 437 | 443 | 449 | 455 | 461 | 467 | 473 | 479 | 485 | |
| 16 | 491 | 497 | 503 | 509 | 516 | 522 | 528 | 534 | 540 | 546 | |
| 17 | 552 | 558 | 564 | 570 | 576 | 582 | 588 | 594 | 600 | 606 | |
| 18 | 612 | 618 | 625 | 631 | 637 | 643 | 649 | 655 | 661 | 667 | |
| 19 | 673 | 679 | 685 | 691 | 697 | 703 | 709 | 715 | 721 | 727 | |
| 720 | 733 | 739 | 745 | 751 | 757 | 763 | 769 | 775 | 781 | 788 | |
| 21 | 794 | 800 | 806 | 812 | 818 | 824 | 830 | 836 | 842 | 848 | |
| 22 | 854 | 860 | 866 | 872 | 878 | 884 | 890 | 896 | 902 | 908 | |
| 23 | 914 | 920 | 926 | 932 | 938 | 944 | 950 | 956 | 962 | 968 | |
| 24 | 85 974 | 980 | 986 | 992 | 998 | *004 | *010 | *016 | *022 | *028 | |
| 25 | 86 034 | 040 | 046 | 052 | 058 | 064 | 070 | 076 | 082 | 088 | |
| 26 | 094 | 100 | 106 | 112 | 118 | 124 | 130 | 136 | 141 | 147 | |
| 27 | 153 | 159 | 165 | 171 | 177 | 183 | 189 | 195 | 201 | 207 | |
| 28 | 213 | 219 | 225 | 231 | 237 | 243 | 249 | 255 | 261 | 267 | |
| 29 | 273 | 279 | 285 | 291 | 297 | 303 | 308 | 314 | 320 | 326 | |
| 730 | 332 | 338 | 344 | 350 | 356 | 362 | 368 | 374 | 380 | 386 | |
| 31 | 392 | 398 | 404 | 410 | 415 | 421 | 427 | 433 | 439 | 445 | |
| 32 | 451 | 457 | 463 | 469 | 475 | 481 | 487 | 493 | 499 | 504 | |
| 33 | 510 | 516 | 522 | 528 | 534 | 540 | 546 | 552 | 558 | 564 | |
| 34 | 570 | 576 | 581 | 587 | 593 | 599 | 605 | 611 | 617 | 623 | |
| 35 | 629 | 635 | 641 | 646 | 652 | 658 | 664 | 670 | 676 | 682 | |
| 36 | 688 | 694 | 700 | 705 | 711 | 717 | 723 | 729 | 735 | 741 | |
| 37 | 747 | 753 | 759 | 764 | 770 | 776 | 782 | 788 | 794 | 800 | |
| 38 | 806 | 812 | 817 | 823 | 829 | 835 | 841 | 847 | 853 | 859 | |
| 39 | 864 | 870 | 876 | 882 | 888 | 894 | 900 | 906 | 911 | 917 | |
| 740 | 923 | 929 | 935 | 941 | 947 | 953 | 958 | 964 | 970 | 976 | |
| 41 | 86 982 | 988 | 994 | 999 | *005 | *011 | *017 | *023 | *029 | *035 | |
| 42 | 87 040 | 046 | 052 | 058 | 064 | 070 | 075 | 081 | 087 | 093 | |
| 43 | 099 | 105 | 111 | 116 | 122 | 128 | 134 | 140 | 146 | 151 | |
| 44 | 157 | 163 | 169 | 175 | 181 | 186 | 192 | 198 | 204 | 210 | |
| 45 | 216 | 221 | 227 | 233 | 239 | 245 | 251 | 256 | 262 | 268 | |
| 46 | 274 | 280 | 286 | 291 | 297 | 303 | 309 | 315 | 320 | 326 | |
| 47 | 332 | 338 | 344 | 349 | 355 | 361 | 367 | 373 | 379 | 384 | |
| 48 | 390 | 396 | 402 | 408 | 413 | 419 | 425 | 431 | 437 | 442 | |
| 49 | 448 | 454 | 460 | 466 | 471 | 477 | 483 | 489 | 495 | 500 | |
| 750 | 87 506 | 512 | 518 | 523 | 529 | 535 | 541 | 547 | 552 | 558 | |
| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |

7
1 0.7
2 1.4
3 2.1
4 2.8
5 3.5
6 4.2
7 4.9
8 5.6
9 6.3

6
1 0.6
2 1.2
3 1.8
4 2.4
5 3.0
6 3.6
7 4.2
8 4.8
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5
1 0.5
2 1.0
3 1.5
4 2.0
5 2.5
6 3.0
7 3.5
8 4.0
9 4.5

| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------------------------|-----|-----|--------|-----|-----|------|------|------|------|------|------|------|
| | | 750 | 87 506 | 512 | 518 | 523 | 529 | 535 | 541 | 547 | 552 | 558 |
| | | 51 | 564 | 570 | 576 | 581 | 587 | 593 | 599 | 604 | 610 | 616 |
| | | 52 | 622 | 628 | 633 | 639 | 645 | 651 | 656 | 662 | 668 | 674 |
| | | 53 | 679 | 685 | 691 | 697 | 703 | 708 | 714 | 720 | 726 | 731 |
| | | 54 | 737 | 743 | 749 | 754 | 760 | 766 | 772 | 777 | 783 | 789 |
| | | 55 | 795 | 800 | 806 | 812 | 818 | 823 | 829 | 835 | 841 | 846 |
| | | 56 | 852 | 858 | 864 | 869 | 875 | 881 | 887 | 892 | 898 | 904 |
| | | 57 | 910 | 915 | 921 | 927 | 933 | 938 | 944 | 950 | 955 | 961 |
| | | 58 | 87 967 | 973 | 978 | 984 | 990 | 996 | *001 | *007 | *013 | *018 |
| | | 59 | 88 024 | 030 | 036 | 041 | 047 | 053 | 058 | 064 | 070 | 076 |
| | | 760 | 081 | 087 | 093 | 098 | 104 | 110 | 116 | 121 | 127 | 133 |
| | | 61 | 138 | 144 | 150 | 156 | 161 | 167 | 173 | 178 | 184 | 190 |
| | | 62 | 195 | 201 | 207 | 213 | 218 | 224 | 230 | 235 | 241 | 247 |
| | | 63 | 252 | 258 | 264 | 270 | 275 | 281 | 287 | 292 | 298 | 304 |
| 1 2 3 4 5 6 | 0.6 | 64 | 309 | 315 | 321 | 326 | 332 | 338 | 343 | 349 | 355 | 360 |
| | 1.2 | 65 | 366 | 372 | 377 | 383 | 389 | 395 | 400 | 406 | 412 | 417 |
| | 1.8 | 66 | 423 | 429 | 434 | 440 | 446 | 451 | 457 | 463 | 468 | 474 |
| | 2.4 | 67 | 480 | 485 | 491 | 497 | 502 | 508 | 513 | 519 | 525 | 530 |
| | 3.0 | 68 | 536 | 542 | 547 | 553 | 559 | 564 | 570 | 576 | 581 | 587 |
| | 3.6 | 69 | 593 | 598 | 604 | 610 | 615 | 621 | 627 | 632 | 638 | 643 |
| 7 8 9 | 4.2 | 770 | 649 | 655 | 660 | 666 | 672 | 677 | 683 | 689 | 694 | 700 |
| | 4.8 | 71 | 705 | 711 | 717 | 722 | 728 | 734 | 739 | 745 | 750 | 756 |
| | 5.4 | 72 | 762 | 767 | 773 | 779 | 784 | 790 | 795 | 801 | 807 | 812 |
| | | 73 | 818 | 824 | 829 | 835 | 840 | 846 | 852 | 857 | 863 | 868 |
| | | 74 | 874 | 880 | 885 | 891 | 897 | 902 | 908 | 913 | 919 | 925 |
| | | 75 | 930 | 936 | 941 | 947 | 953 | 958 | 964 | 969 | 975 | 981 |
| | | 76 | 88 986 | 992 | 997 | *003 | *009 | *014 | *020 | *025 | *031 | *037 |
| | | 77 | 89 042 | 048 | 053 | 059 | 064 | 070 | 076 | 081 | 087 | 092 |
| | | 78 | 098 | 104 | 109 | 115 | 120 | 126 | 131 | 137 | 143 | 148 |
| | | 79 | 154 | 159 | 165 | 170 | 176 | 182 | 187 | 193 | 198 | 204 |
| | | 780 | 209 | 215 | 221 | 226 | 232 | 237 | 243 | 248 | 254 | 260 |
| 1 2 3 4 5 6 | 5 | 81 | 265 | 271 | 276 | 282 | 287 | 293 | 298 | 304 | 310 | 315 |
| | 0.5 | 82 | 321 | 326 | 332 | 337 | 343 | 348 | 354 | 360 | 365 | 371 |
| | 1.0 | 83 | 376 | 382 | 387 | 393 | 398 | 404 | 409 | 415 | 421 | 426 |
| | 1.5 | 84 | 432 | 437 | 443 | 448 | 454 | 459 | 465 | 470 | 476 | 481 |
| | 2.0 | 85 | 487 | 492 | 498 | 504 | 509 | 515 | 520 | 526 | 531 | 537 |
| | 2.5 | 86 | 542 | 548 | 553 | 559 | 564 | 570 | 575 | 581 | 586 | 592 |
| 7 8 9 | 3.0 | 87 | 597 | 603 | 609 | 614 | 620 | 625 | 631 | 636 | 642 | 647 |
| | 3.5 | 88 | 653 | 658 | 664 | 669 | 675 | 680 | 686 | 691 | 697 | 702 |
| | 4.0 | 89 | 708 | 713 | 719 | 724 | 730 | 735 | 741 | 746 | 752 | 757 |
| | 4.5 | 790 | 763 | 768 | 774 | 779 | 785 | 790 | 796 | 801 | 807 | 812 |
| | | 91 | 818 | 823 | 829 | 834 | 840 | 845 | 851 | 856 | 862 | 867 |
| | | 92 | 873 | 878 | 883 | 889 | 894 | 900 | 905 | 911 | 916 | 922 |
| | | 93 | 927 | 933 | 938 | 944 | 949 | 955 | 960 | 966 | 971 | 977 |
| | | 94 | 89 982 | 988 | 993 | 998 | *004 | *009 | *015 | *020 | *026 | *031 |
| | | 95 | 90 037 | 042 | 048 | 053 | 059 | 064 | 069 | 075 | 080 | 086 |
| | | 96 | 091 | 097 | 102 | 108 | 113 | 119 | 124 | 129 | 135 | 140 |
| | | 97 | 146 | 151 | 157 | 162 | 168 | 173 | 179 | 184 | 189 | 195 |
| | | 98 | 200 | 206 | 211 | 217 | 222 | 227 | 233 | 238 | 244 | 249 |
| | | 99 | 255 | 260 | 266 | 271 | 276 | 282 | 287 | 293 | 298 | 304 |
| | | 800 | 90 309 | 314 | 320 | 325 | 331 | 336 | 342 | 347 | 352 | 358 |
| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |
|-----|--------|-----|-----|-----|-----|-----|-----|-----|------|------|-------------|
| 800 | 90 309 | 314 | 320 | 325 | 331 | 336 | 342 | 347 | 452 | 358 | |
| 01 | 363 | 369 | 374 | 380 | 385 | 390 | 396 | 401 | 407 | 412 | |
| 02 | 417 | 423 | 428 | 434 | 439 | 445 | 450 | 455 | 461 | 466 | |
| 03 | 472 | 477 | 482 | 488 | 493 | 499 | 504 | 509 | 515 | 520 | |
| 04 | 526 | 531 | 536 | 542 | 547 | 553 | 558 | 563 | 569 | 574 | |
| 05 | 580 | 585 | 590 | 596 | 601 | 607 | 612 | 617 | 623 | 628 | |
| 06 | 634 | 639 | 644 | 650 | 655 | 660 | 666 | 671 | 677 | 682 | |
| 07 | 687 | 693 | 698 | 703 | 709 | 714 | 720 | 725 | 730 | 736 | |
| 08 | 741 | 747 | 752 | 757 | 763 | 768 | 773 | 779 | 784 | 789 | |
| 09 | 795 | 800 | 806 | 811 | 816 | 822 | 827 | 832 | 838 | 843 | |
| 810 | 849 | 854 | 859 | 865 | 870 | 875 | 881 | 886 | 891 | 897 | |
| 11 | 902 | 907 | 913 | 918 | 924 | 929 | 934 | 940 | 945 | 950 | |
| 12 | 90 956 | 961 | 966 | 972 | 977 | 982 | 988 | 993 | 998 | *004 | |
| 13 | 91 009 | 014 | 020 | 025 | 030 | 036 | 041 | 046 | 052 | 057 | |
| 14 | 062 | 068 | 073 | 078 | 084 | 089 | 094 | 100 | 105 | 110 | |
| 15 | 116 | 121 | 126 | 132 | 137 | 142 | 148 | 153 | 158 | 164 | |
| 16 | 169 | 174 | 180 | 185 | 190 | 196 | 201 | 206 | 212 | 217 | |
| 17 | 222 | 228 | 233 | 238 | 243 | 249 | 254 | 259 | 265 | 270 | |
| 18 | 275 | 281 | 286 | 291 | 297 | 302 | 307 | 312 | 318 | 323 | |
| 19 | 328 | 334 | 339 | 344 | 350 | 355 | 360 | 365 | 371 | 376 | |
| 820 | 381 | 387 | 392 | 397 | 403 | 408 | 413 | 418 | 424 | 429 | |
| 21 | 434 | 440 | 445 | 450 | 455 | 461 | 466 | 471 | 477 | 482 | |
| 22 | 487 | 492 | 498 | 503 | 508 | 514 | 519 | 524 | 529 | 535 | |
| 23 | 540 | 545 | 551 | 556 | 561 | 566 | 572 | 577 | 582 | 587 | |
| 24 | 593 | 598 | 603 | 609 | 614 | 619 | 624 | 630 | 635 | 640 | |
| 25 | 645 | 651 | 656 | 661 | 666 | 672 | 677 | 682 | 687 | 693 | |
| 26 | 698 | 703 | 709 | 714 | 719 | 724 | 730 | 735 | 740 | 745 | |
| 27 | 751 | 756 | 761 | 766 | 772 | 777 | 782 | 787 | 793 | 798 | |
| 28 | 803 | 808 | 814 | 819 | 824 | 829 | 834 | 840 | 845 | 850 | |
| 29 | 855 | 861 | 866 | 871 | 876 | 882 | 887 | 892 | 897 | 903 | |
| 830 | 908 | 913 | 918 | 924 | 929 | 934 | 939 | 944 | 950 | 955 | |
| 31 | 91 960 | 965 | 971 | 976 | 981 | 986 | 991 | 997 | *002 | *007 | |
| 32 | 92 012 | 018 | 023 | 028 | 033 | 038 | 044 | 049 | 054 | 059 | |
| 33 | 065 | 070 | 075 | 080 | 085 | 091 | 096 | 101 | 106 | 111 | |
| 34 | 117 | 122 | 127 | 132 | 137 | 143 | 148 | 153 | 158 | 163 | |
| 35 | 169 | 174 | 179 | 184 | 189 | 195 | 200 | 205 | 210 | 215 | |
| 36 | 221 | 226 | 231 | 236 | 241 | 247 | 252 | 257 | 262 | 267 | |
| 37 | 273 | 278 | 283 | 288 | 293 | 298 | 304 | 309 | 314 | 319 | |
| 38 | 324 | 330 | 335 | 340 | 345 | 350 | 355 | 361 | 366 | 371 | |
| 39 | 376 | 381 | 387 | 392 | 397 | 402 | 407 | 412 | 418 | 423 | |
| 840 | 428 | 433 | 438 | 443 | 449 | 454 | 459 | 464 | 469 | 474 | |
| 41 | 480 | 485 | 490 | 495 | 500 | 505 | 511 | 516 | 521 | 526 | |
| 42 | 531 | 536 | 542 | 547 | 552 | 557 | 562 | 567 | 572 | 578 | |
| 43 | 583 | 588 | 593 | 598 | 603 | 609 | 614 | 619 | 624 | 629 | |
| 44 | 634 | 639 | 645 | 650 | 655 | 660 | 665 | 670 | 675 | 681 | |
| 45 | 686 | 691 | 696 | 701 | 706 | 711 | 716 | 722 | 727 | 732 | |
| 46 | 737 | 742 | 747 | 752 | 758 | 763 | 768 | 773 | 778 | 783 | |
| 47 | 788 | 793 | 799 | 804 | 809 | 814 | 819 | 824 | 829 | 834 | |
| 48 | 840 | 845 | 850 | 855 | 860 | 865 | 870 | 875 | 881 | 886 | |
| 49 | 891 | 896 | 901 | 906 | 911 | 916 | 921 | 927 | 932 | 937 | |
| 850 | 92 942 | 947 | 952 | 957 | 962 | 967 | 973 | 978 | 983 | 988 | |
| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |

1 0.6
2 1.2
3 1.8
4 2.4
5 3.0
6 3.6
7 4.2
8 4.8
9 5.4

1 0.5
2 1.0
3 1.5
4 2.0
5 2.5
6 3.0
7 3.5
8 4.0
9 4.5

| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|--|--|-----|--------|-----|------|------|------|------|------|------|------|------|
| <div> <div>6</div> <div>1 0.6</div> <div>2 1.2</div> <div>3 1.8</div> <div>4 2.4</div> <div>5 3.0</div> <div>6 3.6</div> <div>7 4.2</div> <div>8 4.8</div> <div>9 5.4</div> </div> | | 850 | 92 942 | 947 | 952 | 957 | 962 | 967 | 973 | 978 | 983 | 988 |
| | | 51 | 92 993 | 998 | *003 | *008 | *013 | *018 | *024 | *029 | *034 | *039 |
| | | 52 | 93 044 | 049 | 054 | 059 | 064 | 069 | 075 | 080 | 085 | 090 |
| | | 53 | 095 | 100 | 105 | 110 | 115 | 120 | 125 | 131 | 136 | 141 |
| | | 54 | 146 | 151 | 156 | 161 | 166 | 171 | 176 | 181 | 186 | 192 |
| | | 55 | 197 | 202 | 207 | 212 | 217 | 222 | 227 | 232 | 237 | 242 |
| | | 56 | 247 | 252 | 258 | 263 | 268 | 273 | 278 | 283 | 288 | 293 |
| | | 57 | 298 | 303 | 308 | 313 | 318 | 323 | 328 | 334 | 339 | 344 |
| | | 58 | 349 | 354 | 359 | 364 | 369 | 374 | 379 | 384 | 389 | 394 |
| | | 59 | 399 | 404 | 409 | 414 | 420 | 425 | 430 | 435 | 440 | 445 |
| | | 860 | 450 | 455 | 460 | 465 | 470 | 475 | 480 | 485 | 490 | 495 |
| | | 61 | 500 | 505 | 510 | 515 | 520 | 526 | 531 | 536 | 541 | 546 |
| | | 62 | 551 | 556 | 561 | 566 | 571 | 576 | 581 | 586 | 591 | 596 |
| | | 63 | 601 | 606 | 611 | 616 | 621 | 626 | 631 | 636 | 641 | 646 |
| | | 64 | 651 | 656 | 661 | 666 | 671 | 676 | 682 | 687 | 692 | 697 |
| | | 65 | 702 | 707 | 712 | 717 | 722 | 727 | 732 | 737 | 742 | 747 |
| | | 66 | 752 | 757 | 762 | 767 | 772 | 777 | 782 | 787 | 792 | 797 |
| | | 67 | 802 | 807 | 812 | 817 | 822 | 827 | 832 | 837 | 842 | 847 |
| | | 68 | 852 | 857 | 862 | 867 | 872 | 877 | 882 | 887 | 892 | 897 |
| | | 69 | 902 | 907 | 912 | 917 | 922 | 927 | 932 | 937 | 942 | 947 |
| <div> <div>5</div> <div>1 0.5</div> <div>2 1.0</div> <div>3 1.5</div> <div>4 2.0</div> <div>5 2.5</div> <div>6 3.0</div> <div>7 3.5</div> <div>8 4.0</div> <div>9 4.5</div> </div> | | 870 | 93 952 | 957 | 962 | 967 | 972 | 977 | 982 | 987 | 992 | 997 |
| | | 71 | 94 002 | 007 | 012 | 017 | 022 | 027 | 032 | 037 | 042 | 047 |
| | | 72 | 052 | 057 | 062 | 067 | 072 | 077 | 082 | 086 | 091 | 096 |
| | | 73 | 101 | 106 | 111 | 116 | 121 | 126 | 131 | 136 | 141 | 146 |
| | | 74 | 151 | 156 | 161 | 166 | 171 | 176 | 181 | 186 | 191 | 196 |
| | | 75 | 201 | 206 | 211 | 216 | 221 | 226 | 231 | 236 | 240 | 245 |
| | | 76 | 250 | 255 | 260 | 265 | 270 | 275 | 280 | 285 | 290 | 295 |
| | | 77 | 300 | 305 | 310 | 315 | 320 | 325 | 330 | 335 | 340 | 345 |
| | | 78 | 349 | 354 | 359 | 364 | 369 | 374 | 379 | 384 | 389 | 394 |
| | | 79 | 399 | 404 | 409 | 414 | 419 | 424 | 429 | 433 | 438 | 443 |
| | | 880 | 448 | 453 | 458 | 463 | 468 | 473 | 478 | 483 | 488 | 493 |
| | | 81 | 498 | 503 | 507 | 512 | 517 | 522 | 527 | 532 | 537 | 542 |
| | | 82 | 547 | 552 | 557 | 562 | 567 | 571 | 576 | 581 | 586 | 591 |
| | | 83 | 596 | 601 | 606 | 611 | 616 | 621 | 626 | 630 | 635 | 640 |
| | | 84 | 645 | 650 | 655 | 660 | 665 | 670 | 675 | 680 | 685 | 689 |
| | | 85 | 694 | 699 | 704 | 709 | 714 | 719 | 724 | 729 | 734 | 738 |
| | | 86 | 743 | 748 | 753 | 758 | 763 | 768 | 773 | 778 | 783 | 787 |
| | | 87 | 792 | 797 | 802 | 807 | 812 | 817 | 822 | 827 | 832 | 836 |
| | | 88 | 841 | 846 | 851 | 856 | 861 | 866 | 871 | 876 | 880 | 885 |
| | | 89 | 890 | 895 | 900 | 905 | 910 | 915 | 919 | 924 | 929 | 934 |
| <div> <div>4</div> <div>1 0.4</div> <div>2 0.8</div> <div>3 1.2</div> <div>4 1.6</div> <div>5 2.0</div> <div>6 2.4</div> <div>7 2.8</div> <div>8 3.2</div> <div>9 3.6</div> </div> | | 890 | 939 | 944 | 949 | 954 | 959 | 963 | 968 | 973 | 978 | 983 |
| | | 91 | 94 988 | 993 | 998 | *002 | *007 | *012 | *017 | *022 | *027 | *032 |
| | | 92 | 95 036 | 041 | 046 | 051 | 056 | 061 | 066 | 071 | 075 | 080 |
| | | 93 | 085 | 090 | 095 | 100 | 105 | 109 | 114 | 119 | 124 | 129 |
| | | 94 | 134 | 139 | 143 | 148 | 153 | 158 | 163 | 168 | 173 | 177 |
| | | 95 | 182 | 187 | 192 | 197 | 202 | 207 | 211 | 216 | 221 | 226 |
| | | 96 | 231 | 236 | 240 | 245 | 250 | 255 | 260 | 265 | 270 | 274 |
| | | 97 | 279 | 284 | 289 | 294 | 299 | 303 | 308 | 313 | 318 | 323 |
| | | 98 | 328 | 332 | 337 | 342 | 347 | 352 | 357 | 361 | 366 | 371 |
| | | 99 | 376 | 381 | 386 | 390 | 395 | 400 | 405 | 410 | 415 | 419 |
| | | 900 | 95 424 | 429 | 434 | 439 | 444 | 448 | 453 | 458 | 463 | 468 |
| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |
|-----|--------|------|------|------|------|------|------|------|------|------|-------------|
| 900 | 95 424 | 429 | 434 | 439 | 444 | 448 | 453 | 458 | 463 | 468 | |
| 01 | 472 | 477 | 482 | 487 | 492 | 497 | 501 | 506 | 511 | 516 | |
| 02 | 521 | 525 | 530 | 535 | 540 | 545 | 550 | 554 | 559 | 564 | |
| 03 | 569 | 574 | 578 | 583 | 588 | 593 | 598 | 602 | 607 | 612 | |
| 04 | 617 | 622 | 626 | 631 | 636 | 641 | 646 | 650 | 655 | 660 | |
| 05 | 665 | 670 | 674 | 679 | 684 | 689 | 694 | 698 | 703 | 708 | |
| 06 | 713 | 718 | 722 | 727 | 732 | 737 | 742 | 746 | 751 | 756 | |
| 07 | 761 | 766 | 770 | 775 | 780 | 785 | 789 | 794 | 799 | 804 | |
| 08 | 809 | 813 | 818 | 823 | 828 | 832 | 837 | 842 | 847 | 852 | |
| 09 | 856 | 861 | 866 | 871 | 875 | 880 | 885 | 890 | 895 | 899 | |
| 910 | 904 | 909 | 914 | 918 | 923 | 928 | 933 | 938 | 942 | 947 | |
| 11 | 952 | 957 | 961 | 966 | 971 | 976 | 980 | 985 | 990 | 995 | |
| 12 | 95 999 | *004 | *009 | *014 | *019 | *023 | *028 | *033 | *038 | *042 | |
| 13 | 96 047 | 052 | 057 | 061 | 066 | 071 | 076 | 080 | 085 | 090 | |
| 14 | 095 | 099 | 104 | 109 | 114 | 118 | 123 | 128 | 133 | 137 | |
| 15 | 142 | 147 | 152 | 156 | 161 | 166 | 171 | 175 | 180 | 185 | |
| 16 | 190 | 194 | 199 | 204 | 209 | 213 | 218 | 223 | 227 | 232 | |
| 17 | 237 | 242 | 246 | 251 | 256 | 261 | 265 | 270 | 275 | 280 | |
| 18 | 284 | 289 | 294 | 298 | 303 | 308 | 313 | 317 | 322 | 327 | |
| 19 | 332 | 336 | 341 | 346 | 350 | 355 | 360 | 365 | 369 | 374 | |
| 920 | 379 | 384 | 388 | 393 | 398 | 402 | 407 | 412 | 417 | 421 | |
| 21 | 426 | 431 | 435 | 440 | 445 | 450 | 454 | 459 | 464 | 468 | |
| 22 | 473 | 478 | 483 | 487 | 492 | 497 | 501 | 506 | 511 | 515 | |
| 23 | 520 | 525 | 530 | 534 | 539 | 544 | 548 | 553 | 558 | 562 | |
| 24 | 567 | 572 | 577 | 581 | 586 | 591 | 595 | 600 | 605 | 609 | |
| 25 | 614 | 619 | 624 | 628 | 633 | 638 | 642 | 647 | 652 | 656 | |
| 26 | 661 | 666 | 670 | 675 | 680 | 685 | 689 | 694 | 699 | 703 | |
| 27 | 708 | 713 | 717 | 722 | 727 | 731 | 736 | 741 | 745 | 750 | |
| 28 | 755 | 759 | 764 | 769 | 774 | 778 | 783 | 788 | 792 | 797 | |
| 29 | 802 | 806 | 811 | 816 | 820 | 825 | 830 | 834 | 839 | 844 | |
| 930 | 848 | 853 | 858 | 862 | 867 | 872 | 876 | 881 | 886 | 890 | |
| 31 | 895 | 900 | 904 | 909 | 914 | 918 | 923 | 928 | 932 | 937 | |
| 32 | 942 | 946 | 951 | 956 | 960 | 965 | 970 | 974 | 979 | 984 | |
| 33 | 96 988 | 993 | 997 | *002 | *007 | *011 | *016 | *021 | *025 | *030 | |
| 34 | 97 035 | 039 | 044 | 049 | 053 | 058 | 063 | 067 | 072 | 077 | |
| 35 | 081 | 086 | 090 | 095 | 100 | 104 | 109 | 114 | 118 | 123 | |
| 36 | 128 | 132 | 137 | 142 | 146 | 151 | 155 | 160 | 165 | 169 | |
| 37 | 174 | 179 | 183 | 188 | 192 | 197 | 202 | 206 | 211 | 216 | |
| 38 | 220 | 225 | 230 | 234 | 239 | 243 | 248 | 253 | 257 | 262 | |
| 39 | 267 | 271 | 276 | 280 | 285 | 290 | 294 | 299 | 304 | 308 | |
| 940 | 313 | 317 | 322 | 327 | 331 | 336 | 340 | 345 | 350 | 354 | |
| 41 | 359 | 364 | 368 | 373 | 377 | 382 | 387 | 391 | 396 | 400 | |
| 42 | 405 | 410 | 414 | 419 | 424 | 428 | 433 | 437 | 442 | 447 | |
| 43 | 451 | 456 | 460 | 465 | 470 | 474 | 479 | 483 | 488 | 493 | |
| 44 | 497 | 502 | 506 | 511 | 516 | 520 | 525 | 529 | 534 | 539 | |
| 45 | 543 | 548 | 552 | 557 | 562 | 566 | 571 | 575 | 580 | 585 | |
| 46 | 589 | 594 | 598 | 603 | 607 | 612 | 617 | 621 | 626 | 630 | |
| 47 | 635 | 640 | 644 | 649 | 653 | 658 | 663 | 667 | 672 | 676 | |
| 48 | 681 | 685 | 690 | 695 | 699 | 704 | 708 | 713 | 717 | 722 | |
| 49 | 727 | 731 | 736 | 740 | 745 | 749 | 754 | 759 | 763 | 768 | |
| 950 | 97 772 | 777 | 782 | 786 | 791 | 795 | 800 | 804 | 809 | 813 | |
| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Prop. Parts |

1 5
 2 0.5
 3 1.0
 4 1.5
 5 2.0
 6 2.5
 7 3.0
 8 3.5
 9 4.0
 4.5

1 4
 2 0.4
 3 0.8
 4 1.2
 5 1.6
 6 2.0
 7 2.4
 8 2.8
 9 3.2
 3.6

| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|--|------|--------|-----|-----|------|------|------|------|------|------|------|
| <div> <div>1</div> <div>2</div> <div>3</div> <div>4</div> <div>5</div> <div>6</div> <div>7</div> <div>8</div> <div>9</div> </div> <div> <div>0.5</div> <div>1.0</div> <div>1.5</div> <div>2.0</div> <div>2.5</div> <div>3.0</div> <div>3.5</div> <div>4.0</div> <div>4.5</div> </div> | | 950 | 97 772 | 777 | 782 | 786 | 791 | 795 | 800 | 804 | 809 | 813 |
| | | 51 | 818 | 823 | 827 | 832 | 836 | 841 | 845 | 850 | 855 | 859 |
| | | 52 | 864 | 868 | 873 | 877 | 882 | 886 | 891 | 896 | 900 | 905 |
| | | 53 | 909 | 914 | 918 | 923 | 928 | 932 | 937 | 941 | 946 | 950 |
| | | 54 | 97 955 | 959 | 964 | 968 | 973 | 978 | 982 | 987 | 991 | 996 |
| | | 55 | 98 000 | 005 | 009 | 014 | 019 | 023 | 028 | 032 | 037 | 041 |
| | | 56 | 046 | 050 | 055 | 059 | 064 | 068 | 073 | 078 | 082 | 087 |
| | | 57 | 091 | 096 | 100 | 105 | 109 | 114 | 118 | 123 | 127 | 132 |
| | | 58 | 137 | 141 | 146 | 150 | 155 | 159 | 164 | 168 | 173 | 177 |
| | | 59 | 182 | 186 | 191 | 195 | 200 | 204 | 209 | 214 | 218 | 223 |
| | | 960 | 227 | 232 | 236 | 241 | 245 | 250 | 254 | 259 | 263 | 268 |
| | | 61 | 272 | 277 | 281 | 286 | 290 | 295 | 299 | 304 | 308 | 313 |
| | | 62 | 318 | 322 | 327 | 331 | 336 | 340 | 345 | 349 | 354 | 358 |
| | | 63 | 363 | 367 | 372 | 376 | 381 | 385 | 390 | 394 | 399 | 403 |
| | | 64 | 408 | 412 | 417 | 421 | 426 | 430 | 435 | 439 | 444 | 448 |
| | | 65 | 453 | 457 | 462 | 466 | 471 | 475 | 480 | 484 | 489 | 493 |
| | | 66 | 498 | 502 | 507 | 511 | 516 | 520 | 525 | 529 | 534 | 538 |
| | | 67 | 543 | 547 | 552 | 556 | 561 | 565 | 570 | 574 | 579 | 583 |
| | | 68 | 588 | 592 | 597 | 601 | 605 | 610 | 614 | 619 | 623 | 628 |
| | | 69 | 632 | 637 | 641 | 646 | 650 | 655 | 659 | 664 | 668 | 673 |
| | | 970 | 677 | 682 | 686 | 691 | 695 | 700 | 704 | 709 | 713 | 717 |
| | | 71 | 722 | 726 | 731 | 735 | 740 | 744 | 749 | 753 | 758 | 762 |
| | | 72 | 767 | 771 | 776 | 780 | 784 | 789 | 793 | 798 | 802 | 807 |
| | | 73 | 811 | 816 | 820 | 825 | 829 | 834 | 838 | 843 | 847 | 851 |
| | | 74 | 856 | 860 | 865 | 869 | 874 | 878 | 883 | 887 | 892 | 896 |
| | | 75 | 900 | 905 | 909 | 914 | 918 | 923 | 927 | 932 | 936 | 941 |
| | | 76 | 945 | 949 | 954 | 958 | 963 | 967 | 972 | 976 | 981 | 985 |
| | | 77 | 98 989 | 994 | 998 | *003 | *007 | *012 | *016 | *021 | *025 | *029 |
| | | 78 | 99 034 | 038 | 043 | 047 | 052 | 056 | 061 | 065 | 069 | 074 |
| | | 79 | 078 | 083 | 087 | 092 | 096 | 100 | 105 | 109 | 114 | 118 |
| | | 980 | 123 | 127 | 131 | 136 | 140 | 145 | 149 | 154 | 158 | 162 |
| <div> <div>1</div> <div>2</div> <div>3</div> <div>4</div> <div>5</div> <div>6</div> <div>7</div> <div>8</div> <div>9</div> </div> <div> <div>0.4</div> <div>0.8</div> <div>1.2</div> <div>1.6</div> <div>2.0</div> <div>2.4</div> <div>2.8</div> <div>3.2</div> <div>3.6</div> </div> | | 81 | 167 | 171 | 176 | 180 | 185 | 189 | 193 | 198 | 202 | 207 |
| | | 82 | 211 | 216 | 220 | 224 | 229 | 233 | 238 | 242 | 247 | 251 |
| | | 83 | 255 | 260 | 264 | 269 | 273 | 277 | 282 | 286 | 291 | 295 |
| | | 84 | 300 | 304 | 308 | 313 | 317 | 322 | 326 | 330 | 335 | 339 |
| | | 85 | 344 | 348 | 352 | 357 | 361 | 366 | 370 | 374 | 379 | 383 |
| | | 86 | 388 | 392 | 396 | 401 | 405 | 410 | 414 | 419 | 423 | 427 |
| | | 87 | 432 | 436 | 441 | 445 | 449 | 454 | 458 | 463 | 467 | 471 |
| | | 88 | 476 | 480 | 484 | 489 | 493 | 498 | 502 | 506 | 511 | 515 |
| | | 89 | 520 | 524 | 528 | 533 | 537 | 542 | 546 | 550 | 555 | 559 |
| | | 990 | 564 | 568 | 572 | 577 | 581 | 585 | 590 | 594 | 599 | 603 |
| | | 91 | 607 | 612 | 616 | 621 | 625 | 629 | 634 | 638 | 642 | 647 |
| | | 92 | 651 | 656 | 660 | 664 | 669 | 673 | 677 | 682 | 686 | 691 |
| | | 93 | 695 | 699 | 704 | 708 | 712 | 717 | 721 | 726 | 730 | 734 |
| | | 94 | 739 | 743 | 747 | 752 | 756 | 760 | 765 | 769 | 774 | 778 |
| | | 95 | 782 | 787 | 791 | 795 | 800 | 804 | 808 | 813 | 817 | 822 |
| | | 96 | 826 | 830 | 835 | 839 | 843 | 848 | 852 | 856 | 861 | 865 |
| | | 97 | 870 | 874 | 878 | 883 | 887 | 891 | 896 | 900 | 904 | 909 |
| | | 98 | 913 | 917 | 922 | 926 | 930 | 935 | 939 | 944 | 948 | 952 |
| | | 99 | 957 | 961 | 965 | 970 | 974 | 978 | 983 | 987 | 991 | 996 |
| | | 1000 | 00 000 | 004 | 009 | 013 | 017 | 022 | 026 | 030 | 035 | 039 |
| Prop. Parts | | N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

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